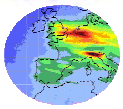
Transport and Transformation of Pollutants (T&TP)
Access to Emission Data, Access to Laboratory Data,
Aerosols, Remote Sensing from Space (AT2),
BIAFLUX, Modelling



AT2

BIAFLUX

The Impact of Climate Change on Air Quality

The 4th ACCENT Barnsdale Expert Workshop

Peter Builtjes, David Fowler, Johann Feichter, Alastair Lewis,
Paul Monks and Peter Borrell
Editors

ACCENT Secretariat
Urbino, March 2008

Report 1.2008

ACCENT Reports

The following reports are published by the ACCENT Secretariat. Further information can be obtained from *http://www.accent-network.org/*.

1.2005 Frontiers in the Transport and Transformation of Pollutants; the Report of the Barnsdale Expert Meeting, 2004, editors, Paul Monks and Peter Borrell, 2005

2.2005 The Remote Sensing of Atmospheric Constituents from Space; the AT2 Strategy Document; editors: John Burrows and Peter Borrell, 2005.

3.2005 Atmospheric Transport and Transformation at Urban and Local Scales; the Report of the Valencia Workshop, 2005; editors N. Moussiopoulos and E.-A. Kalognomou, 2005

4.2005 L'ARIA (Italian version of the booklet: AIR, a short story to walk a long way) by Frank Raes, 2005

5.2005 Challenges in Training and Education (T&E), Position Paper 2005, editor: Evi Schuepbach, 2005

6.2005 Tropospheric Sounding from Space; ACCENT-TROPOSAT-2 in 2004-5; editors: John Burrows and Peter Borrell, 2005.

7.2005 Constituents of Organic Aerosols Workshop Report, Editors Christian Dye, Cathrine Lund Myhre

1. 2006 Trace Gas and Aerosol Flux Measurement Techniques ACCENT- BIAFLUX Workshop Report, Editors David Fowler and Jennifer Muller

2.2006 Towards Robust European Air Pollution Policies: Constraints and Prospects for a wider dialogue between scientists, experts, decision-makers and citizens ASTA-ACCENT Workshop Report, Authors P. Grennfelt, L. Lindau, R. Maas, G. Sundqvist, R. Lidskog, F. Raes, J. Arnell

3.2006 Understanding and quantifying the atmospheric nitrogen cycle; the 2nd ACCENT Barnsdale Expert Meeting, 2005, Editors R.A. Cox, David Fowler, Paul Monks, 2006 and Peter Borrell

4.2006 Common Issues between Air Quality & Climate Change: Research & Policy Recommendations Report Produced by the ACCENT Joint Research Programme on Aerosols: Air quality & Climate, Editors Hans-Christen Hansson and Colin D. O'Dowd

5.2006 Answers to the Urbino Questions, ACCENTs First Policy-Driven Synthesis, Editors Frank Raes and Jens Hjorth

6.2006 Free-Radicals in the Troposphere: Measurement, Interpretation of Field-Data, and Future Directions, Editor Dwayne Heard

7.2006 Chemical Data Assimilation for the Observation of the Earth's Atmosphere, ACCENT/WMO Expert Workshop in support of IGACO, 2006 editors Leonard Barry, John P. Burrows, Paul Monks and Peter Borrell

8.2006 Air Quality in Eastern Europe: Review of Measurement and Modelling Practices and Needs, An ACCENT Expert Meeting, 2006 editors, Claire Granier, Paul Monks, Oksana Tarasova, Semra Tuncel and Peter Borrell.

9.2006 European on-line particle mass spectrometry, report of the Workshop held 29th-30th of November 2005 at JRC-Ispra, Italy editors, D. Mira Salama, J. Hjorth, C. Grüning, N. R. Jensen, M. Dall'Osto.

1.2007 Remote Sensing of Tropospheric Composition from Space; ACCENT-TROPOSAT2 in 2005-6; editors: John Burrows and Peter Borrell, 2007.

2.2007 Proceedings of the Workshop on Model Benchmarking and Quality Assurance, editors, Nicolas Moussiopoulos, Ivar Isaksen.

3.2007 въздухът, малка книжка за да стигнем надалеч. Bulgarian translation by Antoaneta Yotova, Ekaterina Batcharova, Tatiana Spassova, e Maria Koparova of the booklet "AIR" by Frank Raes, 2007.

4.2007 Volatile Organic Compounds in the Polluted Atmosphere, the 3rd ACCENT Barnsdale Expert Meeting, 2007. Editors, John Burrows, Tony Cox, David Fowler, Claire Granier, Ivar Isaksen, Paul Monks, Colin O'Dowd and Peter Borrell.

5.2007 ACCENT Training Workshop and Hellenic Day Hellenic Report 9-12 October 2006, Thessaloniki, Greece. Editors: N. Moussiopoulos, T. Slini, E. Schuepbach

6.2007 Observing Tropospheric Trace Constituents from Space; ACCENT-TROPOSAT-2 in 2006-7; editors: John Burrows and Peter Borrell, 2007.

7.2007 Surface Emissions and Prediction of Atmospheric Composition Changes, Report of The ACCENT-GEIA Summer School, September 11-20, 2007, Ile d'Oléron, France. Editors: Claire Granier, Alex Guenther, Paulette Middleton and Aude Mieville

Produced by: P & PMB Consultants
Newcastle-under-Lyme, Staffordshire, U.K.

Printed by: Keele Graphic Services
Keele University, Staffordshire, U.K.

Impact of Climate Change on Air Quality

4th ACCENT Barnsdale Expert Workshop

Table of Contents

Impact of Climate Change on Air Quality

4th ACCENT Barnsdale Expert Workshop

1. Executive Summary

Climate change is already upon us – the first 2007 IPCC Scientific Report provides near certainty that it is happening together with ample evidence to show that it is induced by human activities. Climate change is a consequence of the increased concentrations of CO_2 and other radiatively active trace gases together with particulate matter in the global atmosphere. The overall effect is to entrap energy in the lower atmosphere, increasing the average surface temperature, increasing the intensity of the circulation and probably changing the general pattern of the weather systems themselves, with direct consequences for us who live on the surface.

Air quality depends the trace gas emissions from the biosphere and from human activities, the chemical reactions which govern the concentrations of trace species in the atmosphere, and on the temperature and the weather systems.. All these processes will be affected by the changes in temperature and circulation, so air quality is likely to be subject to appreciable changes as well. And this is added to the probable increases in human-produced emissions due to the necessary increases in industrial activity as we attempt to cope with the Earth's ever increasing population.

While some qualitative effects of climate change on air quality can be imagined, the detailed response for any particular place or region is far from clear. In the future, the majority of the parameters within the models used to encompass our understanding of air quality will change as the climate changes, as will the emissions and the land use which governs many of them. Whether the models which have been developed and tested within the present climate are flexible enough to cope with the changes is, necessarily, an open question. Thus much intensive research work, both observational and modelling, will be required to ensure that our understanding keeps pace with the changes so that, if possible, more extreme consequences can be predicted and possibly avoided.

It was within this context that the ACCENT 4th Barnsdale expert workshop on the Impact of Climate Change on Air Quality (CCAQ) was initiated. The workshop was held under the auspices of six ACCENT groups: Access to Emission Data, Access to Laboratory Data, Aerosols, Remote Sensing from Space (AT2), BIAFLUX, Modelling, and Transport and Transformation of Pollutants (T&TP). The meeting was held at the Barnsdale Hall Hotel in Rutland on Monday to Wednesday, the 5th to the 7th of November 2007. Some 45 experts attended. (*Appendix 1*).

The meeting was organised around four discussion groups, addressing the major areas of concern. The workshop (*Appendix 2*) started with a plenary talk on each topic. The major part of the meeting was taken up with group discussions, the participants reassembling to consider the recommendations from each group. The speakers, chairs, rapporteurs and participants received detailed instructions to try to ensure that the discussions were as productive as possible (*Appendix* 3). The following conclusions and recommendations emerged from the three discussion groups.

1.1 Investigating changes in photo-oxidants, precursors and feedback mechanisms

1.1.1 Emissions

* Scenarios should be developed which not only take into account actual and direct future anthropogenic and biogenic emissions but which also try to implement downstream human-induced changes related to emission control and land-use change.
* *In situ* and remote measurement techniques for the analysis of the whole range of biogenic VOCs (i.e. isoprene, monoterpenes, sesquiterpenes) should be developed in order to give a longer term perspective on change in the oxidative environment.
* Emission inventories for biogenic VOCs should be improved both on the spatial and temporal scale and be expanded to include speciated terpenoids of higher carbon number.
* Usage of satellites to assess both natural and biogenic emissions of VOCs (*e.g. via* oxidation products) should be seen as a key tool in detecting directly climate induced responses with influence on photo-oxidants.
* Potential emissions in hitherto remote regions, for example new shipping routes in the Arctic ("North-West Passage") should be explored and their long-range impact on the European and US boundary-layer concentrations should be fully explored.
* Usage of *in situ* and remote measurements to observe land-use change related to a warmer climate (due to natural processes and anthropogenic activities (bio fuel production/sequestration) should be integrated fully with biogenic emissions inventories.

1.1.2 Chemical processes

* Continuous measurements of tracer compounds should be used for determination of changes related to the long term trends in reactivity of the atmosphere by *in situ* and remote techniques. Potential candidates are:
    - peroxides and their precursors,
    - HCHO,
    - PAN,
    - organic nitrates, and
    - oxygenated VOCs
* Development of improved structure activity relationship (SARs), to model degradation pathways and reactivities especially for the higher molecular biogenic compounds, such as terpenes and sesquiterpenes are required.
* Development and validation of Arrhenius expressions for rate constants over wider temperature ranges than at present is needed.
* Investigation of reaction rates of $RONO_2$ (organic nitrates) with higher carbon number.
* Investigation of exact reaction pathways of alkoxy radicals (isomerisation/degradation).
* Development of atmospheric chemistry models (regional and global) capable of handling reactions at increased temperatures, say up to 40 ^{o}C.

1.1.3 Dynamics

* Combination of satellite and ground-based observations to detect changes in dynamic processes in the atmosphere.
* The use of explicit models to explain and forecast air pollution issues, rather than adapting numerical weather forecast models for this purpose.
* Knowledge of the vertical distribution of air pollutants and information on boundaries between different lower layers of the atmosphere and exchange processes should be improved.
* The use of continuous vertical observation platforms should be enforced and extended to reactive photochemical species. Examples are: long-term aircraft campaigns (*e.g.* CARIBIC), balloon soundings, zeppelins, and the use of high-tower networks.

1.1.4 General

Heat wave events, such as those experienced in Europe in 2003, can be important in guiding our thinking and understanding of photochemistry in future climates [Schar *et al*., 2004]. Observations in such events are limited to only those made continuously and those where there is serendipitous coincidence of short-term activity with extreme event.

* The European capacity to undertake responsive and short-term detailed observation and modelling campaigns of extreme pollution episodes should be enhanced.

1.2 Investigating changes in surface-atmosphere interactions

1.2.1 Oceans and ice

* To better predict the impact of climate change on polar and especially Arctic air quality, improved modelling of sea ice dynamics is required. Measurement campaigns and a continuous monitoring of surface halogen and O_3 concentrations are recommended to complement satellite data.

1.2.2 Soils

* Future research should address extreme events that are likely to affect soil water content significantly such as floods and droughts, as these are predicted to occur more frequently.
* Freeze-thaw events are known to trigger spring-time N_2O emission pulses, and as permafrost recedes there is likelihood that wider areas will be affected by this phenomenon, warranting further studies.
* More field data are needed to demonstrate whether wetland CH_4 emissions are already responding to climate change, and more generally the global CH_4 budget should be better understood and quantified.
* Integrated research efforts should bring together different scientific communities and projects that are currently focusing, with too little interaction, on fields as wide-ranging as satellite data, remote sensing and process understanding.

1.2.3 Vegetation

* Since major global change factors such as CO_2, O_3, drought and temperature are known to influence the biogenic source strength of VOCs, the short- and long-term responses of VOC emissions to each factor and to their combinations are required as a priority.

* To better quantify national and global source strengths of VOCs at present and in future, it is crucial to develop spatially resolved vegetation/land-use and speciation maps at different spatial scales, forming a reliable basis to assess future projected changes. Spatially and temporally disaggregated hydrometeorological data are also needed to quantify biogenic emissions.

* An improved understanding of species specific compensation points in vegetation for NH_3 and oxygenated VOCs for dominant plant species and land management in the model domain is necessary. Coupled predictive meteorological - VOC emission - air chemistry - transport models should be developed for studying the impact of biogenic sources on air quality, incorporating biogenic processes on shorter timescales, for application on small as well as larger spatial scales.

* For the assessment of ozone damage to vegetation, and feedback effects on trace gas exchange, there clearly is a need to develop a new assessment tool based on ozone uptake by plants, rather than the currently used AOT40 exposure approach.

1.2.4 Land use changes: biomass burning, urbanization, agriculture

* The response of biomass burning to climate change needs to be quantified. Research is needed on the net climatic and air quality impacts of biofuel production and use within the framework of integrated studies.

* As major land use changes are expected in the tropics, current and future trends of biogenic VOC emissions from tropics and their speciation should be assessed. In all these research areas, improved land use datasets (finer spatial resolution, better speciation) are required both for present conditions and projected changes.

* As megacities develop and since current global estimates of anthropogenic VOC emissions are based on data from very few selected countries from the northern hemisphere, speciated anthropogenic VOC emissions globally need to be quantified at different spatial scales, more particularly in developing countries.

1.2.5 Atmospheric processes: turbulence, energy partitioning, hydrometeorology

* At present the consensus on effects of climate change on the frequency of summer-time air quality episodes is that the frequency will increase, but there are many uncertainties, and studies to tackle this issue need to integrate many of the aspects, including increased urbanization to agricultural land use changes, and the need for speciated anthropogenic and biogenic VOCs data to coupled meteorological-emission-chemistry-transport models. At the ecosystem level, a better understanding of chemical reactions on vegetation surfaces and inside the canopy air space is needed.

1.3 Investigating changes in aerosols and their precursors

Air quality and climate science questions meet on regional scales, and it is on these scales that key questions of boundary layer dynamics, convection, and stability and cloud processes and their simulation, including formation, frequency, extent and precipitation, must be better understood. For example processing of aerosols by clouds and wet deposition requires accurate prediction of the cloud and precipitation frequency and amount.

1.3.1 Inorganic aerosol

* Work is needed on to identify current and future trends in nitrate aerosol distributions which depend on the free ammonia availability as well as temperature.

* An improved understanding of the roles of sulphur and nitrogen in the formation of organic aerosol is needed to establish the effect on SOA of changing NO_x and SO_2 emissions. This is an important topic for the legislator.

1.3.2 Organic aerosol

* Organic aerosol is important as the sources, chemistry, pathways and biogenic/anthropogenic balance will all respond to future changes in climate change. Furthermore, it is an important component of local air quality and regional aerosol, where between 30-70 % of submicron PM may be organic in nature. Therefore, they present one of the biggest challenges to impacts of climate change on air quality through aerosols. Considering the many uncertainties in the understanding, and the likely increase with climate change, much work is required to elucidate the fundamental processes involved in the formation, processing and precipitation of organic aerosols.

1.2.3 Ultrafine particles

* Whilst the current metric is PM; there is growing evidence that ultrafine particles are important from a human health perspective [Donaldson *et al.*, 2006]. Ultrafine particle formation is observed widely in many areas, however, this is very sensitive to changes in ambient conditions and is highly non-linear with temperature. Considering the potential effects of ultrafine particles on human health, detailed work is needed on their formation and processing.

1.2.4 Aerosols and clouds

* Improved representation of clouds and precipitation processes in global and regional climate models is much needed as well as a better knowledge of aerosol cycling due to cloud and precipitation processes.

1.2.5 Bioaerosols

* Bioaerosols may well be important sources of ice nuclei and the atmosphere could well be an important pathway for disease and allergen transport via aerosol particles. Little is known about bioaerosols and their behaviour in the atmosphere. However, as biological assay methods improve this will be an important area for needed research.

1.4 Building observation and modelling systems to cope with future change

1.4.1 In-situ monitoring

So there are a number of recommendations to make for promoting the implementation of common air quality and climate change infrastructures.

* Encouraging the current initiatives devoted to a better understanding of the possible links between air quality and climate change and promoting their development. Beyond this objective, they should help to establish common measurement and modelling practices and databases, worthwhile for both communities. This is precisely the stake of the project GEOMON funded by the 6th framework program (*www.geomon.eu*).

* Informing and involving users, especially policy makers, who could help support the development of operational networks for monitoring climate change species by, perhaps, providing a regulatory framework.

* Developing synergies around a key common issue for air quality and climate: atmospheric aerosols. Better knowledge of aerosol compounds properties is crucial for elaborating relevant control strategies in both fields.

* Enhancing synergies for the measurement of vertical profiles that are sought by air quality and climate change scientists. Lidars, sonde networks could be designed for both, as well as measurement campaigns based on aircrafts and balloon measurements. This would the raising and highlighting of common issues and developing links between the experts and scientists involved.

1.4.2 Satellite data

The recommendations are as follows.

* Implementing a satellite earth-observation infrastructure based on both GEO (geostationary) and LEO (low earth orbit) approaches. The former is required for air quality purposes which require the monitoring of dedicated areas with a high temporal resolution (as *in-situ* supersites). Probably one satellite of each type (GEO and LEO) would be enough for Europe, extended to 2 LEO and 3 GEO for the world.
* Improving some instruments such as GOME2, especially in terms of spatial resolution. Currently it is about 80 km × 40 km, and a resolution of 20 km × 20 km can be reached for a better representation of air quality species.
* Filling in the technological gap that should hold from 2012 to 2020 between the ENVISAT and post-Met-Op systems. This is necessary for the improvement of CO_2 and CH_4 global monitoring.
* Promoting integrated coupled approaches by data assimilation with *in-situ* data and models that will allow taking the best benefits from satellite data.

1.4.3 Modelling

Modelling is considered as an important approach for air quality assessment especially if it is combined with measurements. It is also the only available mean for simulating future climate, pollution events and for understanding their relationships. Some recommendations for increasing confidence in modelling for policy making applications are as follows.

* Reducing uncertainties in coupled systems (air quality and climate) with a better description of dynamics and chemical processes (vertical exchange, cloud chemistry, aerosol properties, urban meteorology) ;
* Controlling uncertainties describing input parameters in terms of probability distribution functions ;
* Improving emission description and quantification, especially biogenic emissions that are particularly sensitive to climate change ;
* Developing ensemble systems for focused topics (extreme events for instance) to define the range of possible model responses and assess modelling uncertainties ;
* Promoting integrated approaches linking climate, biosphere and atmosphere systems for a better description of fluxes and concentrations.

2. Introduction to the 4th Barnsdale Expert Workshop

2.1 Climate change

Climate change is already upon us – and, although two swallows do not make a summer, the current sequence of the highest average annual temperatures since records began, as well as the apparently more frequent occurrence of events linked to extreme weather, provides ever more convincing evidence of its occurrence. The first 2007 IPCC Scientific Report provides near certainty that it is happening together with ample evidence to show that it is induced by human activities. The two subsequent 2007 IPCC reports indicate the likely dire consequences in the medium and long term. The sceptics have largely disappeared – critics now maintain that the reports are too conservative and the deterioration will be on us sooner, and with worse consequences, than the reports predict.

Climate change is a consequence of the increased concentrations of CO_2 and other radiatively active trace gases, such as CH_4, O_3, CFCs *etc*. and also particulate matter in the global atmosphere. The effect is to reduce the infrared radiation emitted from the Earth into space, cooling the stratosphere and warming the troposphere. Energy is thus trapped within the lower atmosphere and the surface temperature rises to restore the quantity of energy emitted to space. Thus the steady state, in which energy received from the sun roughly equals the loss of energy by radiation into space, is maintained and the earth again remains at a roughly constant, but increased, temperature. However the effect of entrapment of energy is not just on temperature. The weather systems transfer energy through the atmosphere from the tropics towards the poles and the energy contained in these systems must pass through a lower channel in the troposphere with probable consequent increases in the intensity of weather events. In addition, the changes in surface temperatures and energy transfer are probably changing the general pattern of the weather systems themselves, with direct consequences for us who live on the surface.

The immediate short and medium effects of climate change in the temperate regions of the planet are likely to be warmer winters and longer periods of very hot weather in summer. There is likely to be a general increase in the amount of water vapour in the atmosphere which will probably lead to changes in rainfall patterns, and more intense episodes of rain and wind in some areas. However, while it seems as if, where there is presently enough water there will, at times be too much; it is likely that, thanks to the changed circulation patterns, where there is a scarcity of water, there will be too little!

2.2 Response of air quality to climate change

Air quality depends on the weather systems which circulate the air from place to place, the trace gas emissions from the biosphere and from human activities and the chemical reactions which govern the concentrations of trace species in the atmosphere. All of these processes will be affected by the changes in temperature and circulation which will result from climate change, so air quality is likely to appreciable changes as well. Some of the possible effects are as follows.

* Warmer winters may well reduce the high pressure stagnation periods which lead to serious winter pollution.
* Warmer summer temperatures and lengthened growing seasons may increase the production of biogenic compounds, which may result in increased photo-oxidant production.

* Long hot periods in summer are likely to increase photo-oxidant pollution episodes such as that suffered in parts of central and western Europe in 2003.
* Changes in land use, resulting both from climate change itself and the economic responses to it, will bring changes in both biogenic and human-produced emissions.
* Any increases in storm frequency will increase the flash frequency of lightning and the production of NO_x.
* Increased temperature combined in some areas with lower rainfall will increase the incident of serious forest fires and peat burning, increasing the release of pollutants, sometimes on a global scale.
* Increased CO_2 will, for some plant species, reduce the stomatal openings, thus reducing the uptake of pollutants such as ozone. This may be good for the plant, but will maintain an increased concentration of ozone in the air.

And all this added to the increases in human-produced emissions due to the necessary increases in industrial activity as we attempt to cope with the Earth's ever increasing population!

2.3 Understanding future air quality

While some of the qualitative effects of climate change on air quality can be imagined, the detailed response for any particular place or region is far from clear. Our experience of present air quality is encompassed within models that use emission estimates, chemical reaction schemes and our knowledge of plant processes, all within a meteorological framework, to predict concentrations of trace substances and aerosols. To try to ensure reasonable results, the predictions are compared with values obtained at observation stations. However, with such an under-determined problem, it is not possible to validate the models in any mathematical sense. Nevertheless the majority of models work reasonably well within the present context.

In the future, the majority of the parameters within the model will change as the climate changes, as will the emissions and the land use which governs many of them. Whether the models which have been developed and tested within the present climate are flexible enough to cope with the changes is, necessarily, an open question.

Thus much intensive research work is required to ensure that the chemical schemes encompass the changing mix of trace substances and aerosols, that the parameters describing biosphere-atmosphere interactions cope with changing conditions of temperature and humidity and with new biogenic species, and that the models themselves are flexible and are tested under suitable conditions. In addition the input information such as land-use data, biogenic emissions and human-produced emissions, need reviewing and updating as the changes develop.

Finally, it should not be forgotten that the atmospheric sciences have always been and will continue to be observation-driven. As the impact of climate change on air quality increases, it will be through observations that the inadequacies in our understanding are revealed. Thus observational networks and campaigns, together, with improved instrumentation, are essential if the necessary scientific understanding of the atmospheric environment is to be maintained and improved.

2.4 CCAQ Barnsdale Workshop

It was in the context of understanding these expected changes in air quality that the ACCENT 4th Barnsdale expert workshop on the Impact of Climate Change on Air Quality (CCAQ) was initiated. The workshop was held under the auspices of six ACCENT groups: Access to Emission Data, Access to Laboratory Data, Aerosols, Remote Sensing from Space (AT2), BIAFLUX, Modelling, and Transport and Transformation of Pollutants (T&TP). The meeting was held on Monday, Tuesday and Wednesday, the 5th, 6th and 7th of November 2007. Some 45 experts attended (*Appendix 1*).

The aims of the CCAQ Workshop were:

* to identify and review the key uncertainties in ascertaining the likely effects that the changing climate will have on air quality, on regional, local and urban scales; and
* to provide a basis for future collaborative research priorities in this area.

The meeting was organised around guided discussions on four topics:

Topic 1 Investigating changes in photo-oxidants, precursors and feedback mechanisms, with changing temperature and land use.

Topic 2 Investigating changes in surface-atmosphere interactions with changing temperature and land use.

Topic 3 Investigating changes in aerosols and their precursors with changing temperature, humidity and land use.

Topic 4 Building observation and modelling systems to cope with the interactions of air quality and climate change.

The groups were asked to consider the following points in their discussions.

- Each topic should consider the effects of changes in emissions, due to changes in temperature, meteorology and land use.
- While emphasis will be on investigations of potential future changes, topics may include a consideration of the previous hundred years or so.
- The main issues should be emphasised, within the framework of the Strategy on Air Pollution and the new exceedance limits to be imposed.
- Topics should include large scale modelling, simulating changing meteorological fields, as well as detailed modelling and experimental process studies.
- If possible, some attention should be given to how to assess the controls and feedbacks in natural and anthropogenic emissions

The CCAQ workshop (*Appendix 2*) started with a plenary session in which there were invited review papers on each topic. Each was followed by a short response by the Chair of the particular group who formulated the questions to be discussed by that group.

The groups then separated. The discussions within the groups were managed through "voxboxes", short contributions to the topic under discussions.

The final combined plenary session was devoted to reports from the Rapporteurs of each of the Groups and to a general discussion on future directions.

Prior to the meeting, the Speakers, Chairs and Rapporteurs had received detailed instructions to facilitate productive discussion (*Appendix 3*). Each expert participant was

asked to submit a short illustrated account of their contributions for publication in this report. The main burden at the meeting fell on the Rapporteurs who, with help from the Chairs, summarised the discussion and formulated the recommendations.

2.5 The arrangement of the report.

The essential part of the report is the contributions from the four Rapporteurs, giving the recommendations of their respective groups. The reader can then obtain a perspective of each discussion topic from the accounts of the topic overview lectures. The final section contains the written contributions from the individual participants.

It is hoped that from the report, the reader will experience a flavour of the meeting itself, as well as obtaining a clear impression of the necessary development of the field in the near and medium future.

Some group photographs of the participants are appended (*Appendix 4*).

3. Investigating changes in photo-oxidants, precursors and feedback mechanisms, with changing temperature and land use

Rapporteur's summary from Group 1

Rapporteur: Stefan Reimann

Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Air Pollution and Environmental Technology, CH-8600 Duebendorf, Switzerland

Group 1 Participants: *Alastair Lewis (Chair), Solena Turquety (Plenary Speaker), Stefan Reimann (Rapporteur), Ekatarina Batchvarova, Tony Cox, Russ Dickerson, Paul Monks, Stuart Penkett, Oksana Tarasova, Rosa Salvador, Mihalis Vrekousis.*

Plenary lecture: section 9; participants' contributions, section 10.

3.1. Introduction

Climate change induced by emissions of anthropogenic greenhouse gases is gaining an ever increasing level of attention, both within the scientific community and from political stakeholders. The effect of increasing concentrations of greenhouse gases on temperatures and meteorological systems is already covered in a comprehensive way in the IPCC Fourth Assessment Report (AR4). However, the changing climate will also affect the content of reactive trace gases and particles (relevant to air quality) throughout the total atmospheric column. Therefore Group 1 of the Barnsdale 2007 meeting explored possible connections between climate change and photo-oxidants levels, identified relevant processes and gave the recommendations for their future investigation.

The overall working hypothesis is that rising temperatures have the potential to create a more reactive, photo-oxidative environment. This statement is based on the fact that the rates of chemical reactions are generally known to be higher with increasing temperatures via the so-called "Arrhenius Equation". Furthermore, emissions of biogenic reactive gases, which are participants in ozone formation processes (*i.e*. isoprene, monoterpenes), will be higher in a warmer climate. These general tendencies can however be enhanced or lowered by non-linear effects and by competing temperature-dependant processes such as deposition at surfaces. Second order changes of the biogenic emission can occur due the changes of the plant species for particular regions or due to anthropogenic changes of the land-use.

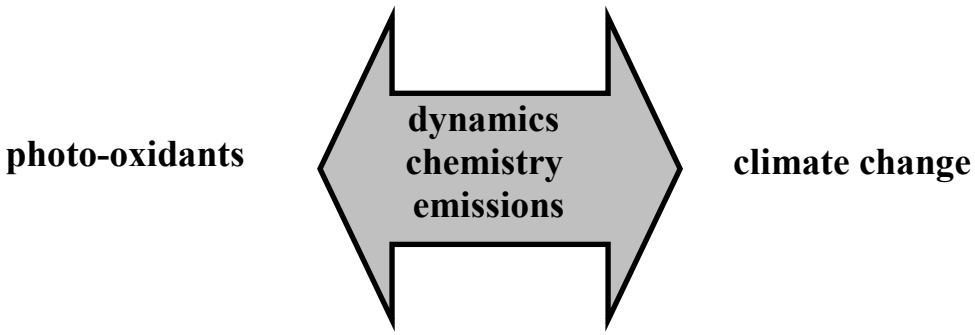


Figure 3.1. Key processes which define the behaviour of photo-oxidants, precursors and feedback mechanisms in a warmer climate.

Furthermore, changes in atmospheric dynamics may be induced by a warmer climate, and these may include both transport patterns and the exchange between the different layers of the atmosphere (*e.g.* stratosphere – troposphere exchange).

Group 1 has identified three key processes, emissions, chemistry, and dynamics, which are involved in the impact of climate change on photo-oxidants, precursors and feedback mechanisms (Figure 3.1). These three processes will be discussed within three separate sections, followed by recommendations regarding future observation platforms, laboratory studies and model approaches to cover changes in the atmospheric composition and dynamics in a warmer climate.

3.2. Changing emissions in a warmer climate

Anthropogenic emissions of precursors have been subject to regulation in developed nations since the interaction of NO_x and VOCs in the production of ozone and other photo-oxidants was first elucidated in the 1950s [Haagen-Smit, 1952]. This has led to a stabilisation or small reductions in peak ozone concentrations within summer pollution events in Europe and other regions. However the response seen in continental ozone levels is not linear with respect to those of the precursors. This illustrates the strongly non-linear behaviour of the atmospheric chemical system. As illustration of the actual state-of-the art Figure 2A shows that, notwithstanding the substantial reductions of NO_x and VOCs that occurred in Switzerland between 1993 and 2006, the correlation of O_3 with the temperature is still almost identical. For the Baltimore area, USA, on the other hand, peak ozone values decreased after a short term and substantial reduction in NO_x due to regulation from power plants (Figure 2B).

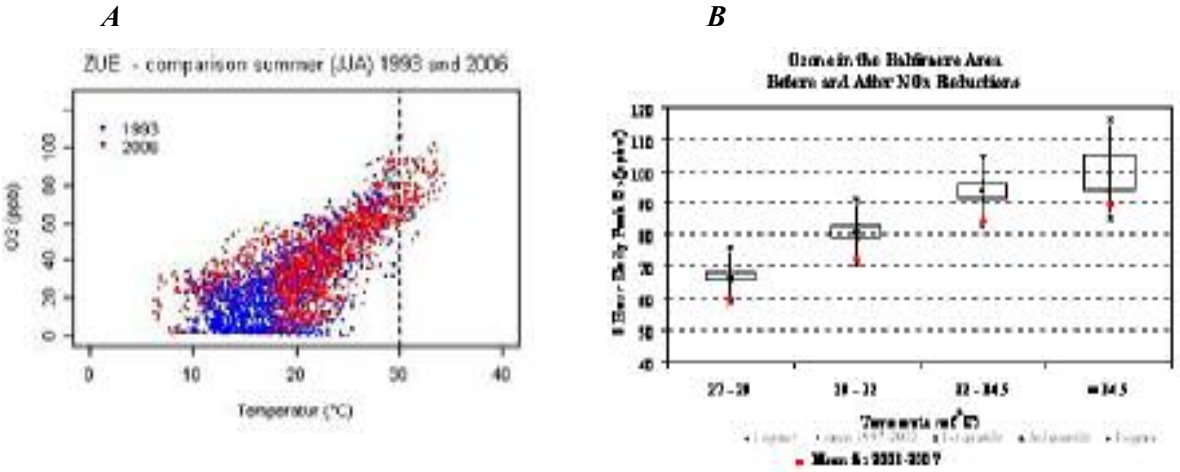


Figure 3.2. A: Concentrations of O_3 vs. temperature during summer in Zurich, Switzerland, 1993 and 2006. B: Differences in 8-h maximum values in Baltimore, USA, between 1987-02 and 2003-06.

In spite of the different response of emission abatements the figure shows a well-established phenomenon of more elevated O_3 concentrations formation with higher temperatures in summertime regardless of location. This is an important issue regarding O_3 behaviour in a warmer climate. A possible scenario could be that although emissions of anthropogenic precursors will be lower, a part of this positive development could be compensated by higher biogenic emissions due to the warmer climate.

Another important issue related to emissions in a warmer climate, which can be due to both natural and anthropogenically induced land-use change: model results for the Eastern US show that plant species will shift northwards and therefore the predominant

maple trees, which are moderate isoprene emitters, will possibly be replaced by oak trees with relatively high emissions of isoprene (Figure 3.3).

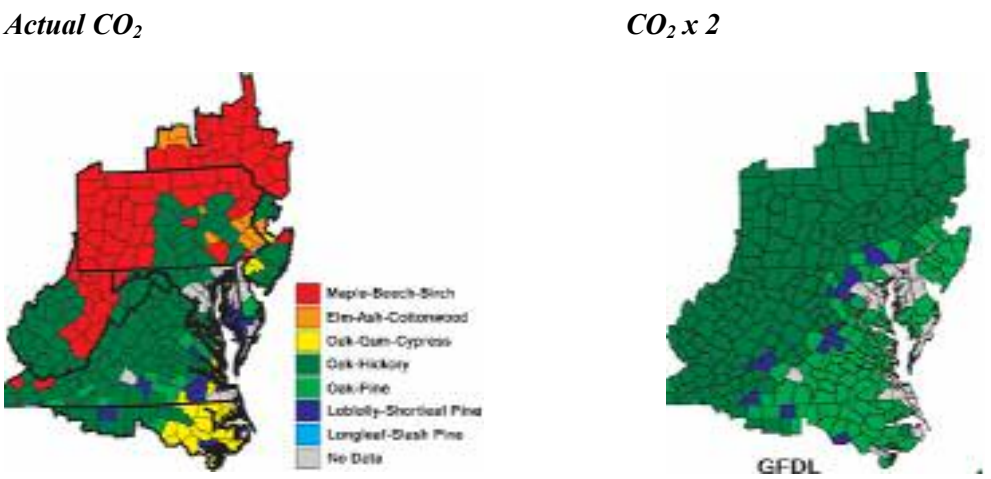


Figure 3.3. Potential effects of increasing temperature on tree species in eastern USA [McKenney-Easterling *et al*., 2000].

Similarly, anthropogenic activities may also affect biogenic emissions for example when natural ecosystems are displaced by species for carbon sequestration or for bio fuel production (*e.g.* palm oil trees). In both cases emissions of the respective areas may change, with follow-on influences on regional air pollution. An important issue in this respect is that information about emissions of biogenic VOCs (*i.e.* isoprene and terpenes) remains patchy both in respect of emissions from specific plant species and from different regions of the world. Especially, knowledge about emissions and behaviour of the fast reacting sesquiterpenes should be improved. For biogenic emissions and their degradation products, satellites are able to fill important gaps especially for global coverage of emissions and for locating hot-spot areas [Millet *et al.*, 2006; Wittrock *et al.,* 2006]. This development should be reinforced.

In general, instruments and models will have to be adapted to document the changes for air pollution induced by climate change. Scenarios should be developed which do not only take into account actual and potential future emissions but also try to indicate human induced changes related to emission control and land-use change.

3.2. Changing chemical processes in a warmer climate

Ever since the occurrence of heavy smog episodes in the urban environments of the west coast of the USA in the 1950s, it has been well-known that air pollution is not only caused by primary pollutants but also by their atmospheric degradation. Indeed secondary air pollution, such as elevated ozone during summer and high concentrations of secondary aerosols in winter has become more important than primary pollutants, such as SO_2, heavy metals and POPs. As an example Figure 3.4 shows a model calculation of very high O_3 concentrations distributed over large regions of Europe during the summer 2003. Furthermore, higher concentrations of $PM_{2.5}$ have been observed during higher temperatures both in winter and summer, although this is only partly represented by model calculations. These particles could provide additional surfaces for heterogeneous reactions which then could change the reactivity. For example, it has been observed that NO_2 on TiO_2 surfaces produces more reactive nitrous acid (HONO).

In general high temperature events such as the "heat-wave summer" 2003 in Europe have the potential to be used to test actual models for their suitability to simulate air pollutants within a future warmer climate.

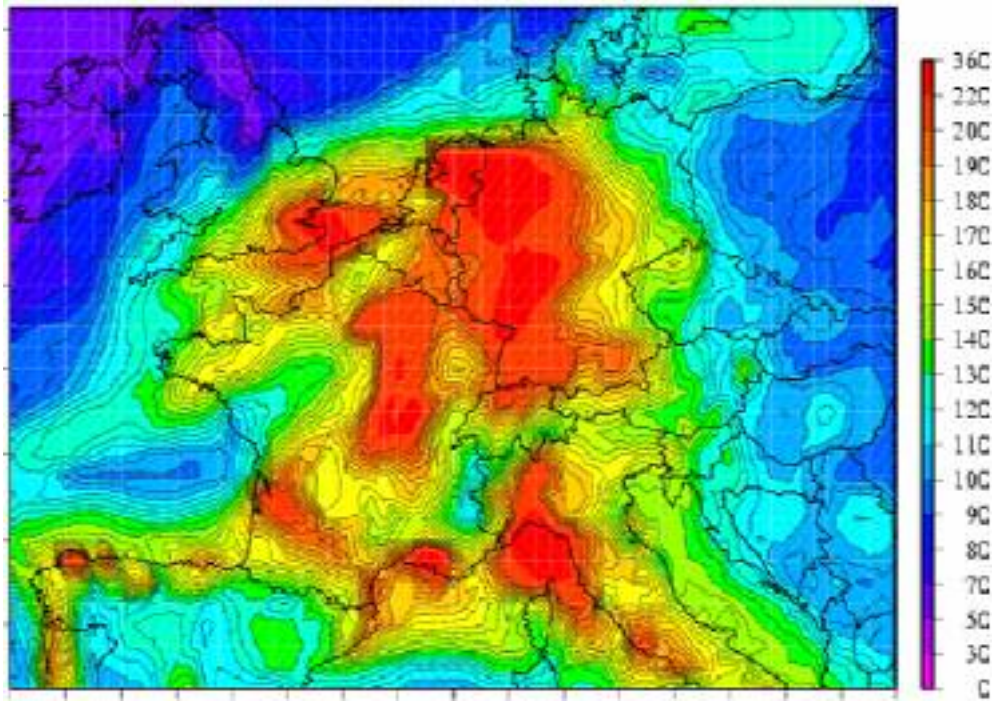


Figure 3.4. Ozone distribution during the heat-wave summer 2003 in Europe.

Specific chemical markers should be measured continuously to assess changes of the atmospheric composition and its ability to transform emissions ("oxidative capacity"). Examples of specific tracers are partly oxidised compounds such as formaldehyde (HCHO), organic nitrates, peroxyacetylnitrate (PAN), or peroxides. Furthermore, ratios of VOCs and oxidised VOCs can be used as tracers to deduce specific processes such as tropospheric ozone decline in the Arctic [Boudries *et al.*, 2002] or the importance of Cl-radical reactions relatively to OH-radical reactions [Hopkins *et al.*, 2002].

In a warmer climate, models will possibly have to be adjusted to cover the new temperature range. Figure 3.5 shows the example of modelled vs. measured O_3 concentrations in the United Kingdom. Modelled and measured values are in good compliance under moderate temperatures. However, during the days with highest temperatures, the model tends to underestimate actual O_3 levels.

Whilst some of this disagreement may be due to a mismatch between emissions and those that are generated from model inventories, it is important to consider alternative sources of potential disagreement. Chemical kinetics are the basis of atmospheric chemical models, so the Arrhenius parameters, where appropriate and applicable, need to be re-examined to cover an environment with higher temperatures. Secondary effects have to be taken into account in addition; it is for example possible that as temperatures rise, direct photolysis may be hindered by increasing cloud cover due to higher evaporation. As it will not be possible to measure the reactivity and degradation pathways for all biogenic VOCs with complex structures such as the sesquiterpenes, the investigation of structure activity relationship (SARs) and their subsequent inclusion into chemical models is a necessity. The final aim would be to include this information into global chemistry-climate models.

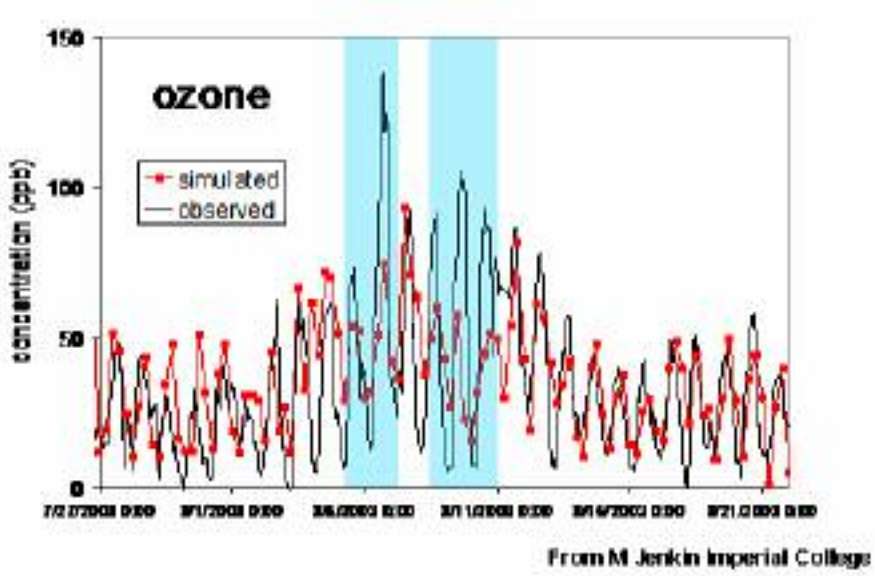


Figure 3.5. Poor model simulations of ozone in high temperature periods (summer 2003, UK).

3.3. Changing dynamics in a warmer climate

Meteorological processes will be influenced by changing climatic conditions. Examples of this phenomenon are the possibility of increased numbers of hurricanes in the US, less winter precipitation as snow fall or a higher probability of heavy rain events in Europe. Furthermore, ocean currents could be influenced by warmer surface water, which then has a feedback onto the climate (*e.g.* possible weakening of the Gulf Stream). Furthermore, the rate of exchange between different layers of the atmosphere and (*e.g.* polluted boundary layer – free troposphere – upper troposphere – stratosphere) is an important feature which has a potential influence on the composition of the atmosphere.

The main application of numerical models which cover dynamic processes in the atmosphere is the weather forecast. However, these models are not necessarily the best option for modelling or forecasting air pollution, since they are generally interested in optimising dynamic parameters (temperature, humidity, wind fields) rather than chemical parameters. For air quality applications, specific information such as the detailed description of the boundary layer has to be presented in a much better way. In other words: predicting extreme weather is probably not the best tool to be used for prediction of the chemical composition of pollution events within future climate.

Natural or anthropogenic land-use change has the potential to influence dynamic processes in the atmosphere. In the western Mediterranean the interaction between marine air masses, land surface (heat and moisture exchanges), and atmospheric pollution (aerosols affecting nucleation), within the sea-breeze circulations can work as a threshold-dominated system. In this system, modest changes in land use and/or air pollution emissions along the coastal areas can change the properties of the air masses and modify the summer storm regime inland. The critical threshold is the height of the cloud condensation level (CCL) of the airmass within the breeze with respect to the height of the coastal mountain ranges [Millán *et al*. 2005].

This situation affects the coasts of north Africa, the Iberian peninsula, southern France and southern Italy, and suggests that land use perturbations, accumulated over historical time and accelerated in the last 30 years, may have induced changes from an open monsoon-type rain regime in the past, with frequent summer storms over the coastal mountains, to one now dominated by closed vertical recirculation and fewer storms. In

the current situation the water vapour remaining in the air and the air pollutants then follow the return flows of the breezes aloft and accumulate over the sea (Figure 3.6).

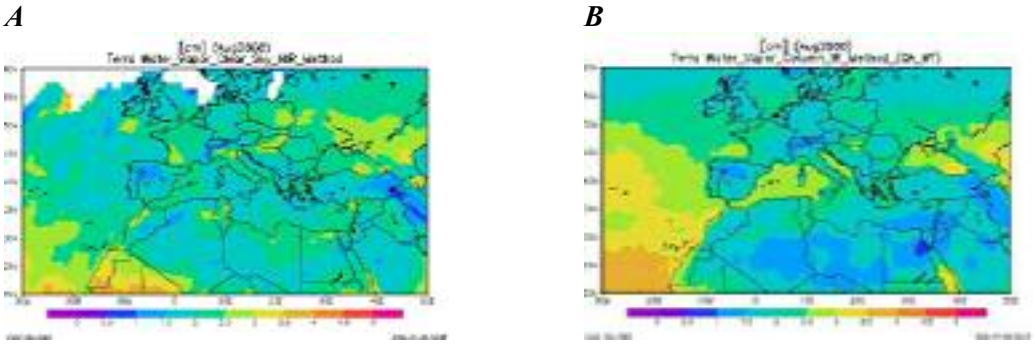


Figure 3.6. Averages of water vapour measurements for August 2000. Water vapour is considered as a tracer for air masses recirculated by the coastal wind system. A: The day product derived at 10:30 UTC emphasises areas where the deep orographic-convection develops at the seabreeze fronts. B: The day plus night product shows the average at 10:30 UTC plus 22:30 UTC, with areas over which water vapour accumulation occurs.

Ground-based measurements and soundings have been used for decades to detect dynamic processes in the atmosphere, and satellites have been used for weather prediction. It is only relatively recently that their potential for detection of dynamic processes related to air pollution transport has begun to be exploited.

To detect changes in dynamics related to climate change, a combination of ground-based measurements and satellite observations should be used. Both of these approaches have their advantages and should be used in combination. *In situ* observations normally have the advantage of providing long-term historic data sets and being relatively reliable in terms of availability and comparability of the data sets. However, geographically distant regions can strongly influence an *in situ* measurements series through changing transport patterns (*i.e.* horizontal advection). This becomes important if long-term changes from specific sites are analysed on the assumption of stable dynamic conditions and regional representativeness. Figure 3.7 gives an example of two long-term data sets of O_3 from two European mountain sites (JFJ: Jungfraujoch (CH) and KHMS, Kislovodsk High Mountain Station (Russia). At Jungfraujoch O_3 exhibits a tendency to grow, whereas at Kislovodsk the trend is negative, especially in 90s. Data analysis in combination with trajectory clusters showed that, in comparison to Jungfraujoch, Kislovodsk was mainly influenced by air masses from the Mediterranean and European Russia, where emissions of precursors are thought to have been reduced more drastically than for western Europe. For the case of JFJ most of arriving air (52 % of cases) originates in eastern USA and spends much time over Atlantic. In this case the trend in the source areas and changing advection patters are the central in interpreting ozone trends rather than local and regional precursor trends.

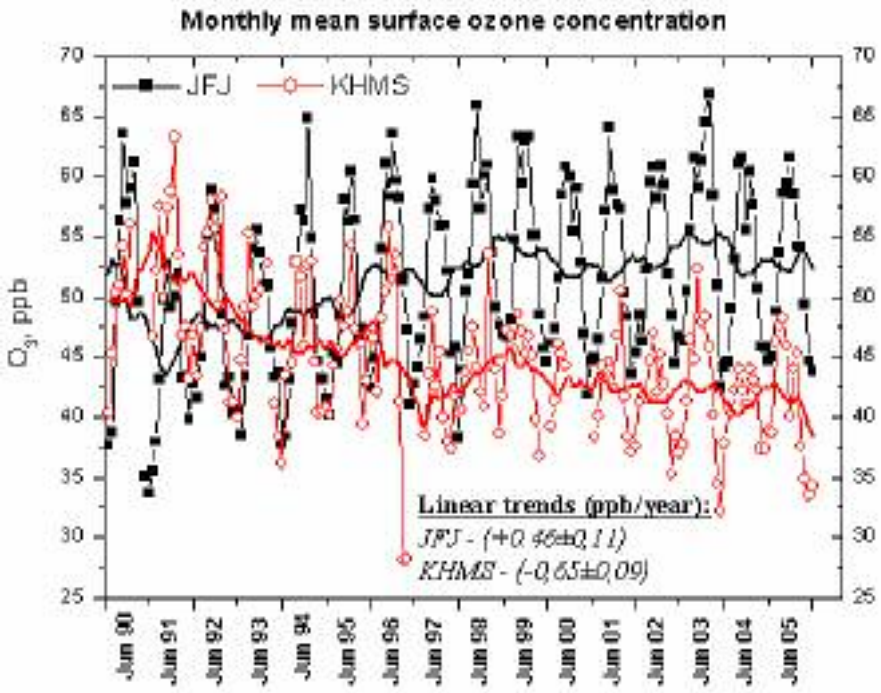


Figure 3.7. O_3 trends at 2 European mountain sites (JFJ: Jungfraujoch, Switzerland; KHMS: Kislovodsk, Russia).

Satellite-based observations provide global coverage but spatial and temporal resolution is limited. Furthermore, long-term availability is not ensured. An example of the satellites application to detect changes in dynamics is given in Figure 3.8. Analysis of 25-year TOMS (Total Ozone Mapping Spectrometer) data has been used to define the position of the Subtropical and Polar Jets [Hudson *et al.*, 2006]. Analysis shows that in eastern USA, Baltimore, the occurrence of the subtropical jet stream has increased, while the occurrence of the polar jet stream has declined. As the subtropical jet stream condition is mostly related to stagnant weather conditions, air pollution has a higher tendency to accumulate.

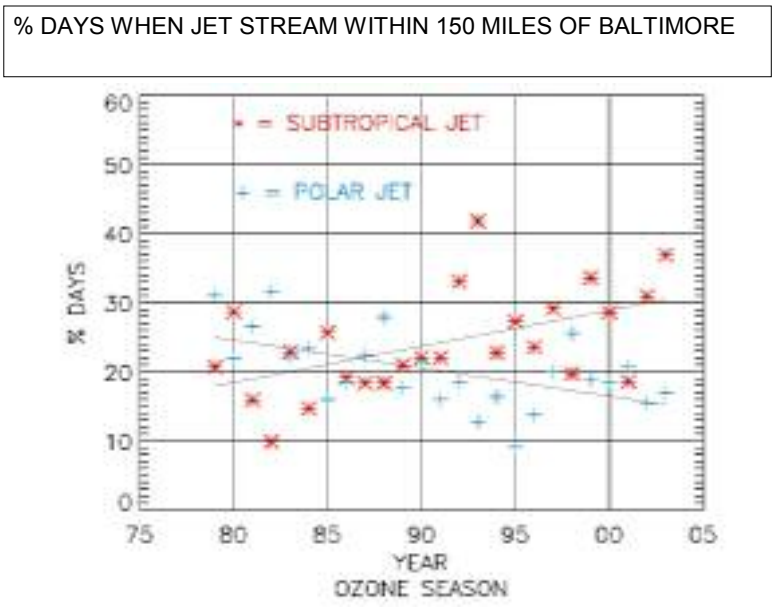


Figure 3.8. Percent of days when polar and subtropical jet streams are within 200 km of Baltimore.

3.4. Recommendations

3.4.1. General recommendation

Heat wave events, such as those experienced in Europe in 2003, can be important in guiding our thinking and understanding of photochemistry in future climates [Schar *et al*., 2004]. Observations in such events are limited to only those made continuously and those where there is serendipitous coincidence of short-term activity with extreme event. Therefore, the European capacity to undertake responsive and short-term detailed observation campaigns should be enhanced to provide a capability to predict future events using the best available instruments and models.

3.4.2. Specific recommendations

1. Emissions

* Scenarios should be developed which not only take into account actual and direct future anthropogenic and biogenic emissions but which also try to implement downstream human-induced changes related to emission control and land-use change.
* *In situ* and remote measurement techniques for the analysis of the whole range of biogenic VOCs (i.e. isoprene, monoterpenes, sesquiterpenes) should be developed in order to give a longer term perspective on change in the oxidative environment.
* Emission inventories for biogenic VOCs should be improved both on the spatial and temporal scale and be expanded to include speciated terpenoids of higher carbon number.
* Usage of satellites to assess both natural and biogenic emissions of VOCs (*e.g. via* oxidation products) should be seen as a key tool in detecting directly climate induced responses with influence on photo-oxidants.
* Potential emissions in hitherto remote regions, for example new shipping routes in the Arctic ("North-West Passage") should be explored and their long-range impact on the European and US boundary layers should be fully explored.
* Usage of *in situ* and remote measurements to observe land-use change related to a warmer climate (due to natural processes and anthropogenic activities (bio fuel production/sequestration) should be integrated fully with biogenic emissions inventories.

2. Chemical processes

* Continuous measurements of tracer compounds should be used for determination of changes related to the long term trends in reactivity of the atmosphere by *in situ* and remote techniques. Potential candidates are:
    - peroxides and their precursors,
    - HCHO,
    - PAN,
    - organic nitrates,
    - oxygenated VOCs.
* Development of improved structure activity relationship (SARs), to model degradation pathways and reactivities especially for the higher molecular biogenic compounds, such as terpenes and sesquiterpenes are required.
* Development and validation of Arrhenius expressions over a wider temperature range is needed.

* Investigation of reaction rates of $RONO_2$ (organic nitrates) with higher carbon number.
* Investigation of exact reaction pathways of alkoxy radicals (isomerisation/degradation).
* Development of atmospheric chemistry models (regional and global) capable of handling reactions in higher temperature range.

3. Dynamics

* Combination of satellite and ground-based observations to detect changes in dynamic processes in the atmosphere.
* Use of specific models to explain/forecast air pollution issues, rather than tuning numerical weather forecast for this purpose.
* Knowledge of the vertical distribution of air pollutants and information on boundaries between different lower layers of the atmosphere and exchange processes should be improved.
* The use of continuous vertical observation platforms should be enforced and extended to reactive photochemical species. Examples are: long-term aircraft campaigns (*e.g.* CARIBIC), balloon soundings, zeppelins, and the use of high-tower networks.

References

Boudries, H., J. W. Bottenheim, C. Guimbaud, A. M. Grannas, P. B. Shepson, S. Houdier, *et al*. 2002. "Distribution and trends of oxygenated hydrocarbons in the high Arctic derived from measurements in the atmospheric boundary layer and interstitial snow air during the ALERT2000 field campaign." *Atmospheric Environment* **36**(15-16): 2573-2583.

Haagen-Smit, A. J., 1952. "Chemistry and Physiology of Los-Angeles Smog." *Industrial and Engineering Chemistry* **44**(6): 1342-1346.

Hopkins, J. R., I. D. Jones, A. C. Lewis, J. B. McQuaid and P. W. Seakins, 2002. "Non-methane hydrocarbons in the Arctic boundary layer." *Atmospheric Environment* **36**(20): 3217-3229.

Hudson, R. D., M. F. Andrade, M. B. Follette and A. D. Frolov, 2006. "The total ozone field separated into meteorological regimes - Part II: Northern Hemisphere mid-latitude total ozone trends." *Atmospheric Chemistry and Physics* **6**: 5183-5191.

McKenney-Easterling, M., D. R. DeWalle, L. R. Iverson, A. M. Prasad and A. R. Buda, 2000. "The potential impacts of climate change and variability on forests and forestry in the Mid-Atlantic Region." *Climate Research* **14**(3): 195-206.

Millan, M. M., M. J. Estrela, M. J. Sanz, E. Mantilla, M. Martin, F. Pastor, *et al.*, 2005. "Climatic feedbacks and desertification: The Mediterranean model." *Journal of Climate* **18**(5): 684-701.

Millet, D. B., D. J. Jacob, S. Turquety, R. C. Hudman, S. L. Wu, A. Fried, *et al.,* 2006. "Formaldehyde distribution over North America: Implications for satellite retrievals of formaldehyde columns and isoprene emission." *Journal of Geophysical Research-Atmospheres* **111**(D24).

Schar, C., P. L. Vidale, D. Luthi, C. Frei, C. Haberli, M. A. Liniger, *et al*., 2004. "The role of increasing temperature variability in European summer heatwaves." *Nature* **427**(6972): 332-336.

Wittrock, F., A. Richter, H. Oetjen, J. P. Burrows, M. Kanakidou, S. Myriokefalitakis, *et al*., 2006. "Simultaneous global observations of glyoxal and formaldehyde from space." *Geophysical Research Letters*, **33** (16).

4. Investigating changes in surface-atmosphere interactions with changing temperature and land use

Rapporteur's summary from Group 2

Rapporteur: C.R. Flechard

Soils, Agronomy and Spatialization (SAS) unit, INRA, 65 rue de St-Brieuc, 35042 Rennes, France

Group 2 Participants: *David Fowler (Chair), Bill Collins (Plenary Speaker), Chris Flechard (Rapporteur), J. Neil Cape, Pierre Cellier, Giacomo Gerosa, Claire Granier, Mari Pihlatie, Kim Pilegaard, Andreas Richter, Rainer Steinbrecher*

Plenary Lecture: section 9; participants' contributions, section 11

4.1. Introduction

The plenary presentation on the effects of climate change on ozone exchange and feedbacks into the carbon cycle was given by W. Collins on behalf of S. Sitch, and a detailed account of the talk is to be found in this report. The presentation set the scene for much of the ensuing discussion in the group and, although focussing on the interactions between tropospheric ozone and surface/atmosphere processes, many generic issues raised here were relevant for a wide range of atmospheric species, both in terms of emissions from and deposition to the Earth's surface. Rather than organizing the group discussions around the various atmospheric compounds in succession, the vox-box presentations and discussions were held during different sessions focussing first on the component parts of the biosphere *i.e.* oceans and freshwater, ice and snow surfaces, soils and vegetation, and then on cross-cutting issues and mechanisms at work when considering land use changes and atmospheric processes.

4.2. Oceans and freshwater/ice/snow surfaces

Polar boundary layer chemistry

Changes in patterns of sea ice formation and melting in the Arctic have been shown to affect polar tropospheric chemistry. For example, severe ozone depletion episodes (ODE) have been observed in springtime over sea ice and more rarely over coastal regions of the Arctic (Figure 4.1), and are linked to elevated concentrations of bromine, leading to depleted concentrations of total gaseous mercury. The complex chemistry involves emission bursts of bromine from preferentially fresh sea ice, possibly involving frost flowers, and subsequent reaction with ozone, to form BrO and HOBr. The reaction of gaseous mercury with BrO and HOBr is thought to be the main pathway of atmospheric mercury depletion, which leads to enhanced dry deposition of oxidized mercury onto snow and ice and enhanced bio-accumulation in the polar ecosystem. Episodes of enhanced BrO (events) are typically triggered in small areas and then "explode" to larger regions, and the effect is local or regional rather than global. As multi-year ice coverage decreases, the probability for frost flowers / first year ice will increase, which may favour bromine explosion events, although direct evidence for a role of frost flowers in Br release has yet to be produced. Similar processes are likely to occur in the Antarctic, but whether halogen emissions increase or decrease in future remains uncertain.

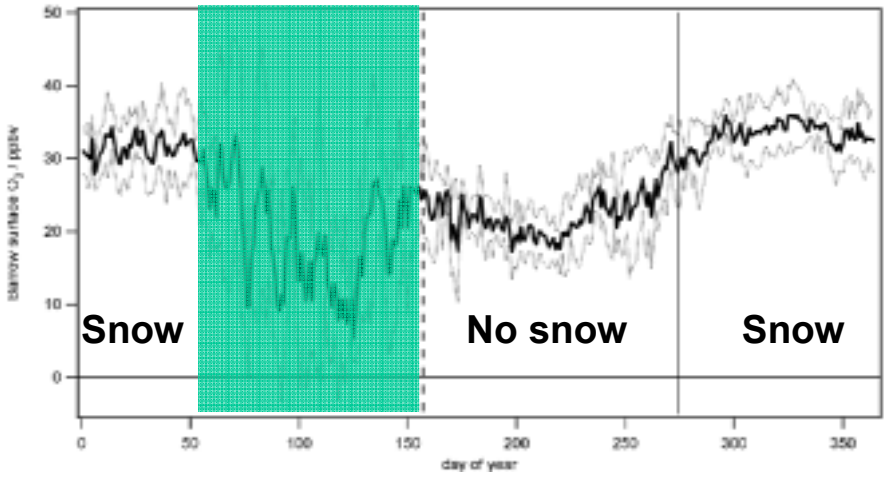


Figure 4.1. Spring-time ozone depletion episode at Barrow (W. Simpson, personal communication, based upon NOAA/ESRL/GMD data).

Increased anthropogenic interferences in the Arctic are likely in future, including industrialization (*e.g.* oil drilling), increased transport and ship emissions, as sea ice cover recedes and new navigation routes open up (*e.g.* the NW Passage). Enhanced dry deposition of black carbon could significantly decrease the albedo of polar ice and thus accelerate melting. Increased anthropogenic emissions into the Arctic boundary layer have the potential to interfere with the halogen chemistry during ODEs, *e.g.* by changing the pH. However, the timing of emissions (summer time) and ozone depletion (spring) is somewhat out of phase.

Oceanic emissions

Dimethyl sulphide (DMS) emissions by oceans are a function of concentration in surface seawater and of wind speed and surface regime (smooth, rough, breaking), where the rough regime accounts for 70 % of situations. Seawater concentrations are expected to increase with temperature, giving rise to increases in emissions, but there is no consensus on the future evolution of surface winds, so that changes in DMS emissions are uncertain. Similarly, marine aerosol originate in sea salt being generated through the action of wind across the sea surface, and the response of the emission to wind speed is highly non-linear, so that predicting changes in wind speeds becomes crucial in assessing the response of marine emissions to climate change. The contribution of anthropogenic nutrients and eutrophication needs also to be considered

Recommendations

To better predict the impact of climate change on polar and especially Arctic air quality, improved modelling of sea ice dynamics is required. Measurement campaigns and a continuous monitoring of surface halogen and O_3 concentrations are recommended to complement satellite data. The analysis of existing data from. the POLARCAT project for example would help elucidate the impact on climate.

4.3. Soils

While soils are sources and/or sinks of a wide range of compounds including NO, N_2O, CH_4, O_3, VOCs, NH_3 and dust, the impact of climate change on soil processes relevant for air quality is likely to be most important for oxidized nitrogen compounds and especially NO with its role as a major precursor of photochemical oxidant production. This was reflected in the predominance of vox-box contributions on NO emissions by soils. However, the greenhouse gas N_2O was also discussed as being another major

nitrogen loss with environmental consequences in the nitrification/denitrification cycle, with soil humidity dictating to a large extent whether NO or N_2O emission dominates.

NO *and* N_2O *emissions*

Recent studies in European forests (*e.g.* the NOFRETETE project) indicate that the fraction of available N in soil emitted as NO/N_2O increases with the eutrophication level, and that NO emissions by soils within coniferous forests are higher than in deciduous forests. The measurements confirm that NO emissions increase non-linearly with temperature (Figure 4.2), so that higher NO losses can be expected in future climates if soil moisture remains constant. The predicted altered precipitation patterns and intensified occurrence of droughts and floods make it more difficult however to assess whether NO or N_2O emission would increase most, given that most NO emission occurs below 60 % water-filled pore space (nitrification-dominated) and most N_2O emission occurs above 60 % water-filled pore space (denitrification-dominated). At natural sites with a low atmospheric nitrogen input, increased soil organic matter mineralization with increasing soil temperature may in time outweigh atmospheric deposition in supplying available N to the root zone, so that in a warming context, oxidized nitrogen emissions would be less limited by the level of nitrogen deposition.

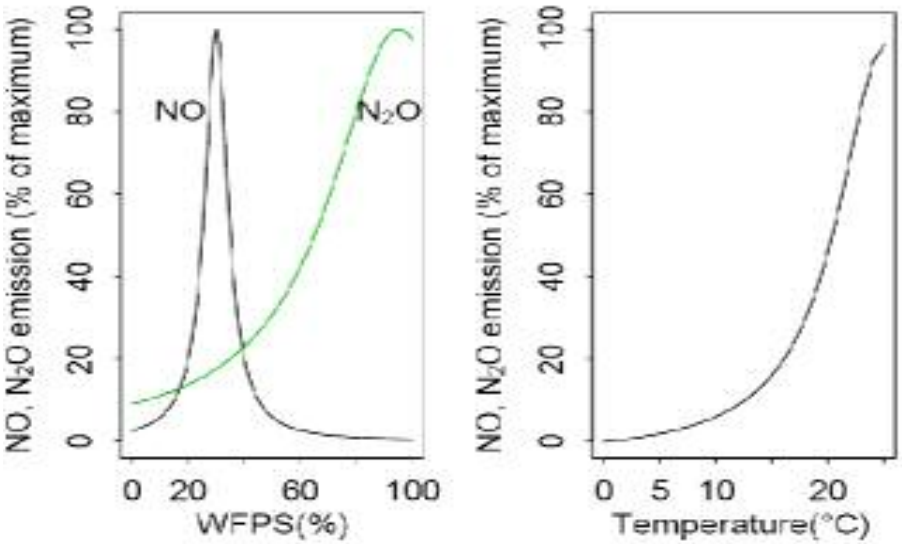


Figure 4.2. Environmental controls of NO and N_2O emissions by forest soils: results of the NOFRETETE project [Pilegaard *et al.*, 2006]. WFPS: volumetric fraction of water-filled pore space in soil.

Model NO emission estimates differ widely nationally, regionally and globally and most of the modelling is empirical, in coupling emissions to temperature and soil water and nitrogen parameters. The development of process-based models to quantify regional emission of NO is limited by the lack of a full understanding of the mechanisms of NO production and consumption in soils and the soils and atmospheric data for up-scaling in time and space. For agricultural areas, farm input data and farming practices impact heavily on the accuracy of model predictions. The timing of fertilizer application especially is crucial, since soil moisture determines the type and intensity of soil microbiological activity, and since the farm manager's decision to apply fertilizer on any given day is often a function of the weather and of soil moisture itself.

CH_4 *emission and oxidation*

With receding permafrost at northern latitudes and increasing boreal areas of wetland, CH_4 emissions are expected to increase with increases in air and surface temperature. The effect would be compounded by a lengthening of the emitting season, and by a

reduction of the CH_4 oxidation capacity of boreal forest soils if soil available N follows an increasing trend, either through increased atmospheric N deposition or enhanced soil organic matter mineralization.

Recommendations

Future research should address extreme events that are likely to affect soil water content significantly such as floods and droughts, as these are predicted to occur more frequently. Freeze-thaw events are known to trigger spring-time N_2O emission pulses, and as permafrost recedes there is a likelihood that there would be wider areas affected by the phenomenon, warranting further studies.

More field data are needed to demonstrate whether wetland CH_4 emissions are already responding to climate change, and more generally the global CH_4 budget should be better understood and quantified. Integrated research efforts should bring together different scientific communities and projects that are currently focusing, with too little interaction, on fields as wide-ranging as satellite data, remote sensing and process understanding.

4.4. Vegetation

Terrestrial vegetation represents an active interface between soil and atmosphere, acting as a source or sink of many atmospheric trace species including NO_2, O_3, SO_2, N_2O, CH_4, VOCs, NH_3 and aerosols. For vascular plants much of the exchange is regulated by stomatal conductance, which will respond to changes in temperature, soil moisture, water vapour pressure deficit and vegetation type or land use. The pollution climate also affects stomatal functioning and leaf surface chemistry.

Changes in stomatal conductance

The temperature response of stomatal conductance (G_s) depends on which side of the optimum temperature for plant growth (T_{opt}) plants are growing. In southern Europe for example, future summer-time temperatures are likely to exceed T_{opt} for a higher fraction of the time and thus result in an increased temperature stress. For example, the 2003 European heat wave and drought, regarded widely as a forerunner of future years, has provided evidence of reduced stomatal uptake of ozone in a long-term study in Italy, where the dry deposition flux to vegetation was reduced by half over the growing season as compared to a normal year (Figure 4.3). Conversely, at northern latitudes temperatures during the growing season would move toward T_{opt}, increasing stomatal conductance. In addition, the lengthening of the growing season at mid and high latitudes would increase the seasonally-cumulated evapo-transpiration and fluxes of trace gases.

Increasing CO_2 concentration is also expected to reduce stomatal conductance, thereby limiting the dry deposition of NO_2, SO_2, O_3 and contributing to an elevation of boundary layer O_3 concentration. The general effect of elevated CO_2 would be a reduction of O_3 uptake by and damage to plants, although the increased boundary layer O_3 concentration and increased plant exposure might exert a negative feed-back on stomatal conductance, the extent of which is uncertain. A consensus has emerged that assessments of plant productivity reductions due to O_3 must be made through quantification of stomatal flux, rather than using an accumulated exposure above threshold concept (AOT40), the response of which to climate change is misleading.

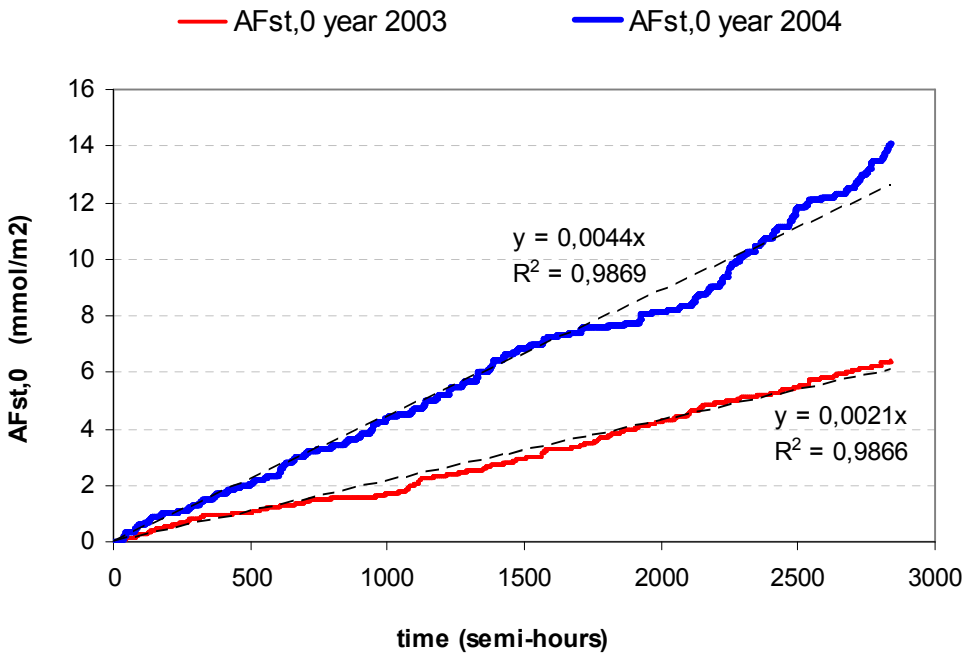


Figure 4.3. Reduction in seasonal (cumulative) O_3 dry deposition to a Holm oak forest in Italy during the 2003 heat wave and drought, compared with a normal year (2004) [Gerosa *et al*., 2008].

Biogenic emissions of trace gases

Global emissions of volatile organic compounds (VOCs) are dominated by biogenic sources, which respond to both climate and land use changes. Biogenic VOC emissions peak in summer in response to elevated temperatures, predominantly (two thirds of the emissions) over forested areas (Figure 4.4), but the speciated source strengths of *e.g.* isoprene, monoterpenes, sequiterpenes and oxygenated VOCs are dependent on tree species, highlighting the need for digital tree species maps with high spatial resolution to be used in modelling.

Biogenic VOC emissions have also been shown in treatment studies to be sensitive to drought and elevated CO_2 and O_3, but plants may evolve over time and adapt to a *gradually* changing environment, so that their actual response to climate change may differ from that predicted on the basis of such studies held over much shorter periods of time.

The influence of vegetation on N_2O and CH_4 emissions remains globally uncertain. For NH_3, the stomatal compensation point in vegetation increases exponentially with temperature, approximately doubling for every 5 to 6 K increase, so that an increase in atmospheric NH_3 concentrations is also expected in future. However, although a better mechanistic understanding of surface/atmosphere NH_3 exchange has been achieved over the last 20 years, the link between fertilizer application or atmospheric N deposition and the actual compensation point of agricultural or natural ecosystems has yet to be resolved quantitatively and applied spatially across landscapes in the modelling domain.

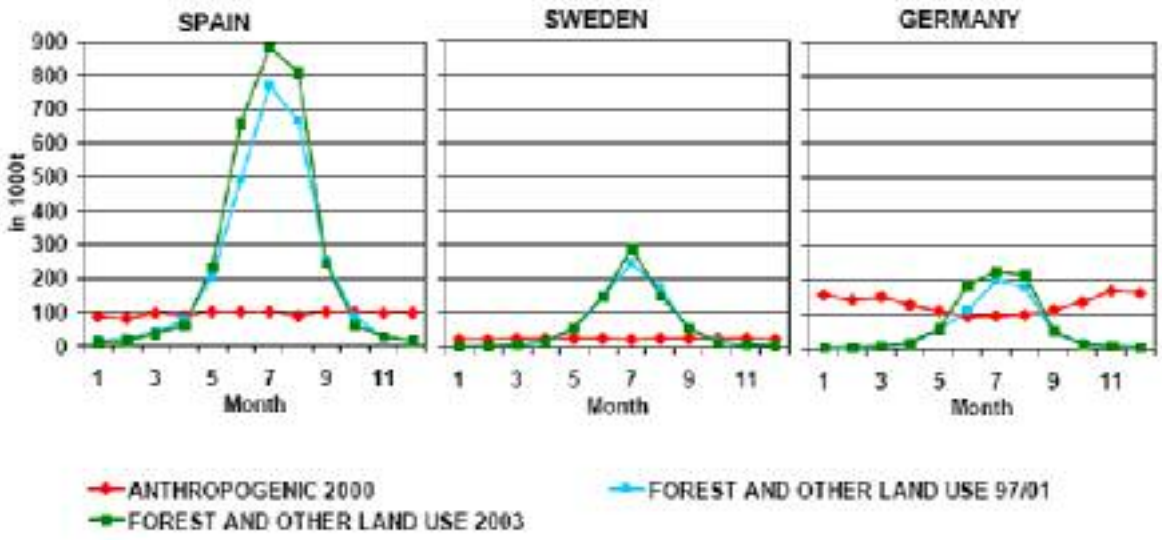


Figure 4.4. Seasonal variability of biogenic and anthropogenic VOC emissions in three European countries (adapted from Friedrich *et al*., 2007). Note the 10 % enhancement of the summer-time emission peak during the 2003 heat wave as compared with the inter-annual mean for 1997-2001.

Leaf surface wetness and chemistry

Much of the atmospheric load of gaseous and particulate pollutants is removed by dry deposition to rough terrestrial surfaces including vegetation. Leaf surface wetness strongly influences the dry deposition of NH_3, SO_2, HNO_3 and other water-soluble species, by reducing the canopy resistance or lowering the canopy compensation point and enhancing uptake by water films. A temperature increase displaces thermodynamic equilibria towards the gas phase and thus reduces the potential for dry deposition to wet surfaces. Further, the response to climate change of spatial and temporal patterns of vegetation wetness distribution is highly uncertain; precipitation events may be less frequent but more intense, followed by faster evaporation and longer dry spells; dewfall patterns may be altered; droughts and floods may occur more frequently but in different geographical locations, so that the net effect on regional or global dry deposition, and on the atmospheric lifetime of trace gases and aerosols, is difficult to predict.

Recommendations

Since major global change factors such as CO_2, O_3, drought and temperature are known to influence the biogenic source strength of VOCs, the short- and long-term responses of VOC emissions to each factor and to their combinations are required as a priority.

To better quantify national and global source strengths of VOCs at present and in future, it is crucial to develop spatially resolved vegetation/land-use and speciation maps at different spatial scales, forming a reliable basis to assess future projected changes. Spatially and temporally disaggregated hydrometeorological data are also needed to quantify biogenic emissions.

An improved understanding of species specific compensation points in vegetation for NH_3 and oxygenated VOCs for dominant plant species and land management in the model domain is necessary. Coupled predictive meteorological -VOC emission - air chemistry - transport models should be developed for studying the impact of biogenic sources on air quality, incorporating biogenic processes with high frequency time steps, for application at small as well as larger spatial scales.

For the assessment of ozone damage to vegetation and feedback effects on trace gas exchange, there clearly is a need to develop a new assessment tool based on ozone uptake by plants, to replace the currently used AOT40 exposure approach.

4.5. Land use changes: biomass burning, urbanization, agriculture

Global changes in land use are expected to occur, primarily as a result of climate change and of the projected increase in world population, both through biogeochemical processes and human management. Land use change will also impact back on climate and on air quality through emissions of greenhouse gases, VOCs and aerosols. The group discussions focused on biomass burning, urbanization and agricultural changes, which are detailed here, but other topics were also mentioned, including for example changes in shrub abundance in Alaska and the uncertain effect on biogenic emissions.

Biomass burning

Biomass burning is a large source of pollution, which has changed historically and will change as a function of land-use and climate. Biomass burning could be larger in the future as a result of more frequent droughts, but changes in forest management also need to be taken into account. Over the 20th century CO_2 emissions from fires are estimated to have decreased in the northern hemisphere and to have increased in the southern hemisphere, especially in S. America and in Africa (Figure 4.5), primarily as a result of changes in land and forest management.

An accurate assessment of global areas burnt today as well as predictions for the future are necessary, but the type of vegetation is also important because it determines the speciation of emissions. For example, carbon dioxide emissions from savanna burning and from forest fires are rather similar per unit area, but for other chemical species emissions factors very different for savannah and forest. As the spatial distribution of vegetation depends on climatic conditions, the accuracy of the quantification of past and future changes determines our ability to assess the impact of biomass burning on air quality.

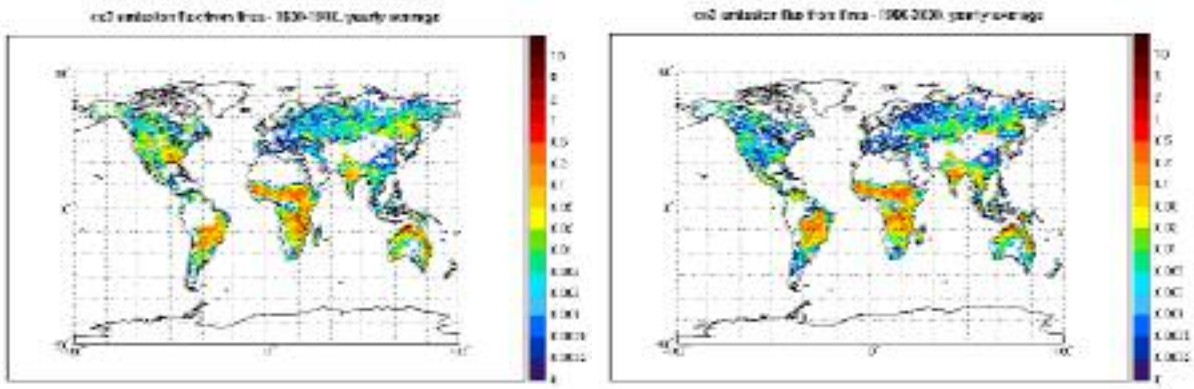


Figure 4.5. Historical changes in global CO_2 emissions from fires. Estimates are shown for the first (left panel) and last (right panel) decades of the 20th century [Mieville *et al.*, 2008].

Urbanization

Megacities have become an emerging chemistry-climate issue during the second half of the 20th century, with many examples across the globe of reduced air quality and visibility, appreciable health effects from elevated concentrations of particulate matter (PM), O_3 and NO_2, and ecosystem damage by emissions of sulfur and nitrogen oxides, NH_3 and VOCs. Although the effect of urbanization is not currently included in GCMs, the conversion to urban land cover also creates urban heat islands associated with

considerable warming [Christensen *et al.*, 2007]. Increasing amounts of air pollution are transported from megacities to the regional and global scales, and will alter spatial and temporal patterns of precipitation, hydrology, temperature and sunshine. Non-linear feedbacks of climate change on the emissions and air quality in megacities and their surroundings are to be expected in the future. Key issues also include the poorly quantified dry deposition rates in cities and the changes in wet deposition downwind.

Agriculture

Land use changes related to agriculture and the need to feed a growing global population are poorly quantified, but will have a large impact on land-atmosphere exchange. The recent development of biofuels caused by dwindling global fossil fuel stocks and increasing oil prices, and the loss of tropical forests to palm oil and soybean farming, are examples of socio-economic and political drivers of land use change that are extremely difficult to quantify in future scenarios. From a mechanistic viewpoint, most of the knowledge in current land-atmosphere exchange models is based predominantly on data from mid to high latitudes with relatively little data for the tropical regions.

Recommendations

The response of biomass burning to climate change needs to be quantified. Research is needed on the net climatic and air quality impacts of biofuel production and use within the framework of integrated studies. As major land use changes are expected in the tropics, current and future trends of biogenic VOC emissions from tropics and their speciation should be assessed. In all these research areas, improved land use datasets (finer spatial resolution, better speciation) are required both for present conditions and projected changes.

As megacities develop and since current global estimates of anthropogenic VOC emissions are based on data from very few selected countries from the northern hemisphere, speciated anthropogenic VOC emissions globally need to be quantified at different spatial scales, more particularly in developing countries.

4.6. Atmospheric processes: turbulence, energy partitioning, hydrometeorology

Contributions to the group on surface/atmosphere exchange have demonstrated that most of the processes which regulate emission/deposition fluxes are very climate sensitive. Temperature in particular strongly influences chemical reactions as well as biological mechanisms and determines the aqueous/gaseous/aerosol partitioning, while playing a role in the control of stomatal conductance in plants. Broadly, it could be argued that most emission terms may be expected to increase with likely changes to climate and land use, while most deposition terms would decrease, but there are exceptions to this pattern.

Atmospheric turbulence determines the maximum exchange rate between vegetation and the atmosphere and the vertical mixing of pollutants in the boundary layer, so that any change in turbulence patterns will affect the frequency and duration of air quality episodes. Another effect of a theoretically enhanced turbulence within the trunk space of forest canopies would be of an increased O_3 deposition to the forest floor, an enhanced NO emission and a reduction of the vertical NO_x gradient. Future changes in surface winds are however a matter of continued debate and there is a large uncertainty on the potential impact of turbulence on air quality and on the re-suspension and deposition of aerosols over land, as well as on the gas and aerosol exchange over oceans.

Climate-related episodes such as droughts, floods, heat waves and storms are on the increase globally [Christensen *et al.*, 2007] and are of special interest not only for air quality, but also for the partitioning of energy and hydrology. If drier summers, higher vapour pressure deficits, higher temperatures and elevated CO_2 and O_3 all combine to reduce stomatal conductance and evapo-transpiration, a higher fraction of the incident precipitation may leave the ecosystem in runoff rather than to the atmosphere, with a potentially increased flood risk. Model simulations by the UK Met Office have shown that the magnitude of the O_3 effect on transpiration is 25 % that of the CO_2 effect [Sitch *et al.*, 2008].

Recommendations

At present the consensus on effects of climate change on the frequency of summer-time air quality episodes is that the frequency will increase, but there are many uncertainties, and studies to tackle this issue need to integrate many of the aspects presented in this report (Figure 4.6), from increased urbanization to agricultural land use changes, and from the need for speciated anthropogenic and biogenic VOCs data to coupled meteorological-emission-chemistry-transport models. At the ecosystem level, a better understanding of chemical reactions on vegetation surfaces and inside the canopy air space is needed.

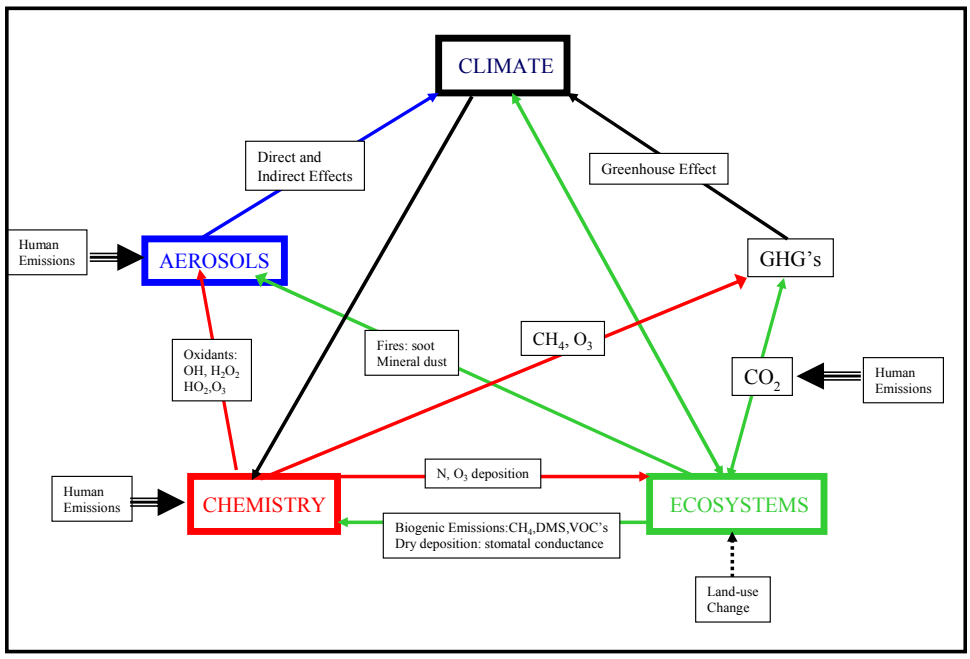


Figure 4.6. The coupled climate system with biosphere/atmosphere feedbacks (P. Cox and W. Collins, personal communication).

References

Christensen, J.H., B. Hewitson, A. Busuioc, A. Chen, X. Gao, I. Held, R. Jones, R.K. Kolli, W.-T. Kwon, R. Laprise, V. Magaña Rueda, L. Mearns, C.G. Menéndez, J. Räisänen, A. Rinke, A. Sarr and P. Whetton, 2007. Regional Climate Projections. In: *Climate Change 2007: The PhysicalScience Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Friedrich, R., Theloke, J., Winiwarter, W., Gebetsroiter, E., Steinbrecher, R., Butterbach-Bahl, K., Smiatek, G., Dore, Ch., Grice, S., Korcz, M., Fudala J., Cruci, G., Beekmann M., Gaudioso, D., Saarnio, S., Seufert, G., Köble, R., Etiope, G., 2008. Natural and biogenic emissions and their impact on air quality. *Proceedings of ACCENT Symposium 2007*, in press.

Gerosa G., Finco A., Mereu S., Vitale M., Manes F., Ballarin Denti A., 2008. Comparison of seasonal variations of ozone exposure and fluxes in a Mediterranean Holm oak forest between the exceptionally dry 2003 and the following year. *Environmental Pollution* (in press).

Mieville *et al.* (2008). Manuscript in preparation.

Pilegaard, K., U. Skiba, P. Ambus, C. Beier, N. Brüggemann, K., Butterbach-Bahl, J. Dick, J. Dorsey, J. Duyzer, M. Gallagher, R. Gasche, L. Horvath, B. Kitzler, A. Leip, M. K. Pihlatie, P. Rosenkranz, G. Seufert, T. Vesala, H. Westrate and S. Zechmeister-Boltenstern, 2006. Nitrogen load and forest type determine soil emission of nitrogen oxides (NO and N_2O). *Proceedings of the 1st iLEAPS Science Conference*, Boulder, January 2006.

Sitch, S. *et al.*, 2008. Manuscript in preparation.

5. Investigating changes in aerosols and their precursors with changing temperature, humidity and land use.

Rapporteur's summary from Group 3

Rapporteur: Hugh Coe

University of Manchester, UK

Plenary Lecture: section 9; participants' contributions, section 12.

5.1 Introduction

Aerosol particles are known to have an deleterious effect on human health and also have a major influence on the Earth's radiation budget by scattering and absorbing incoming short wave radiation and by controlling the microphysical properties of cloud and hence their reflectivity. Although many scientific questions remain, the roles of aerosols in both air quality and climate science have been widely studied though the two areas have tended to be treated rather separately. Climate changes in the future may impact on aerosols and hence have an impact on air quality. This report summarises the discussions of the aerosol working group which focussed on the potential importance of such interactions; identified the main areas where such interactions would occur and offered a series of recommendations for future research in this area.

The two plenary talks on aerosols were presented by Thorsten Hoffman on the impact of Climate Change on Secondary Organic Aerosols and by Johann Feichter on Aerosols, Clouds and Climate Change. The participants presented voxboxes, of which, written accounts are given in section 12

5.2 Behavioural and social changes

Before considering the effects of changing climate on air quality, the group considered the effect of changes in behaviour and social patterns on aerosol particle loadings and air quality. Current world population stands at 6.1 billion people. This is projected to rise to 8.9 billion by 2050, a 50 % increase (WHO, 2004). Energy use will rise commensurately with this increase in population, which will certainly increase particulate emissions and secondary aerosol production without the implementation of new technologies. There has been a shift in population towards urban areas and an increasing number of very large, so-called, megacities, leading to far greater numbers of people exposed to poor air quality. This is likely to increase in the coming decades.

At the present time, most large urban centres are in the mid latitudes in the northern hemisphere. The major increases in population are likely to occur at low latitudes and it is expected that in future, the large megacities experiencing air quality problems will be located in much warmer climates that are exposed to higher levels of radiation. These changes may well give rise to changes in rate or pathway of photochemical processes responsible for the formation of secondary aerosol precursor material.

It is also expected that as population patterns change and fuel availability alters there is likely to be a major shift in fuel use. This will have a significant impact on emissions. It is likely that the use of biofuels will substantially increase. The use of ethanol and other fuels derived from biomass are increasing substantially and have already led to increases in grain prices as agricultural production is no longer driven by food production alone. However, at the present time, particulate emissions from biofuels have not been well quantified. This needs to be resolved as the emissions profiles are

likely to be significantly different from fuel oil emissions. The areas of most rapidly rising population are in the developing world and, at the present time, wood burning is the main fuel used domestically in these areas. This is likely to continue for some time to come and will become more important as population rises. Particulate emissions from wood burning are potentially much higher than those from other combustion sources, though this varies widely depending on the method of burn. More work is required to quantify these emissions sources and their toxicity.

5.3 Effects of climate change on air quality

The recent working group 1 report in the fourth assessment of the Intergovernmental Panel on Climate Change (*http://www.ipcc.ch/pdf/assessment-report/ar4/wg1*) provides a thorough and up to date summary of the likely changes to the Earth's climate and its regional variability over the next 100 years. Some of these changes are discussed in more detail in Feichter's contribution (section 12). Given that this synthesis of the likely changes and their associated uncertainty is the most probable picture of climate change currently available, the group discussed how these predicted changes may affect air quality in the future.

5.3.1 Increasing global temperature, distribution, changes in annual variations

The IPCC [2007] concluded that global temperature increases in the range 2 to 4.5 °C are likely with a best estimate of 3 °C, though the increases are highly emission scenario dependent. However, the warming is expected to be greatest over the land and greater increases are expected at higher latitudes with increases of between 5 and 6.5 °C possible. The IPCC also concluded that it was very likely that extreme heat waves will be become more frequent.

Increasing temperature will lead to increasing volatility of semi-volatile components and consequently a greater partitioning into the gas phase. Ammonium nitrate is at present an important component of particulate matter (PM) in many European, Asian and north American cities. Increased temperatures will lead to an equilibrium favouring greater partitioning to the gas phase as nitric acid and ammonia. This will decrease the total PM loading (Figure 5.1) and will shorten the lifetime of both oxidised and reduced nitrogen in the atmosphere as their deposition is considerably faster than ammonium nitrate in accumulation mode aerosol [Morino *et al*., 2006; Dawson *et al*., 2007]. Primary and secondary organic material is another major contributor to PM in urban environments and has been linked with adverse health effects. The organic fraction may partition as the particulate and its precursors age in the atmosphere. Robinson *et al*. [2007] showed very large improvements in the regional simulation of the particulate organic loading if re-volatilization of semivolatile primary material was accounted for during ageing and dilution. Changes in temperature will significantly affect this distribution. Secondary organic aerosol remains poorly understood, in particular anthropogenic organic aerosol are massively underpredicted by models [Heald *et al*., 2005], recent work has highlighted several possible formation mechanisms and offered evidence that oligomeric formation is prevalent [Rudich *et al*., 2007]. Changes in temperature may affect both the formation pathways and the partitioning of this material and hence affect the SOA burden in urban aerosols.

Increases in temperature are also likely to lead to increases in emissions of precursors. For example, biogenic volatile organic carbon and evaporative emissions of anthropogenic material are likely to increase. As these substances are processed in the atmosphere their products may be much less volatile and re-condense. Soil emissions are known to be highly temperature sensitive and these are also likely to increase. These

effects are very poorly quantified over land surfaces and are not known over oceans at the present time.

Increased temperature will change chemical reaction rates in the atmosphere. For example, Dawson *et al*. [2007] used regional model simulations using PMCAMx chemical transport model to investigate regional PM changes due to a 2.5 °C increase. They showed that whilst ammonium nitrate decreased due to volatilization this was largely offset in summer by enhanced sulfate production in summertime due to the direct increase of reaction rate at increased temperatures but largely from increased oxidant concentration (see section 2). Furthermore, the increases in conversion of SO_2 to sulphate in the eastern USA have the net effect of decreasing the export of sulphate and increasing its deposition of the eastern USA, a change in the overall deposition footprint of sulfur.

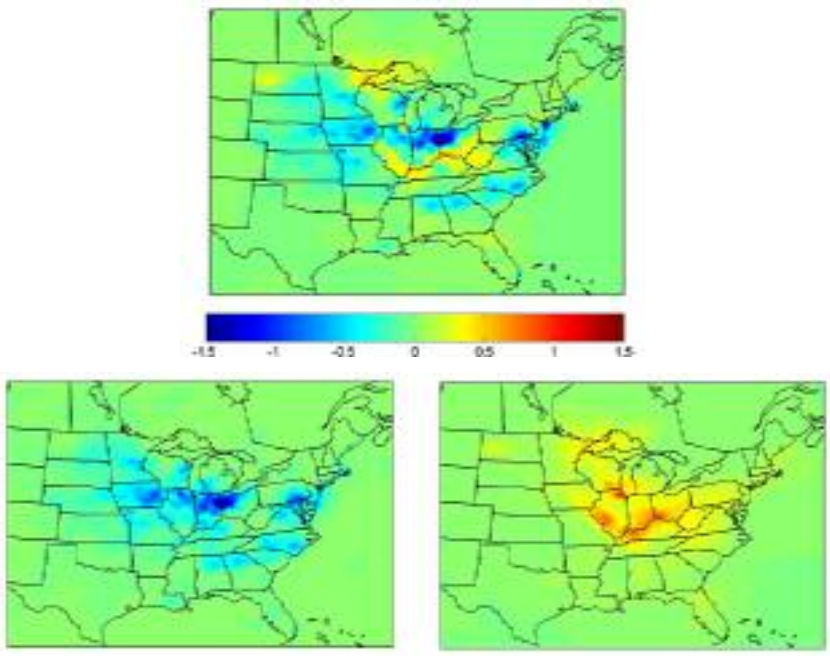


Figure 5.1. Average changes in (a) total $PM_{2.5}$ (μgm^{-3}), (b) $PM_{2.5}$ nitrate, and (c) $PM_{2.5}$ sulfate predicted from the eastern US in July using PMCAMx for a 2.5 K temperature increase [Dawson *et al*., 2007].

Nucleation has been observed in boreal forest [Kulmala *et al*., 2001], coastal [O'Dowd *et al*., 2002], and urban environments [Stanier *et al*., 2004]. Various nucleation processes have been postulated, many of which are highly temperature dependent. As a result, reliable predictions of these highly non linear systems are not possible at the present time.

It is becoming widely recognised that bioaerosols are widely present in the atmosphere. They can act as nuclei for ice crystals and hence influence cloud microphysics. The atmosphere acts as a medium for transport of bioaerosols and this may be an important pathway for disease spread.

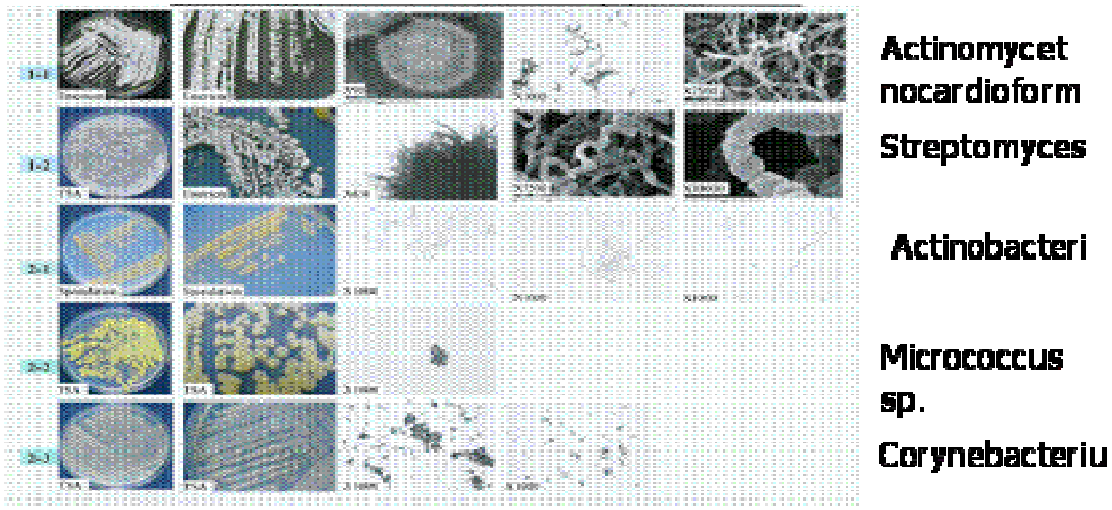


Figure 5.2. Examples of biological particles in cloud water (see Flossmann, page 201)

Temperature increases are likely to change bioaerosol production but at the present time we do not know enough to make projections of future changes and impacts.

5.3.2 Increases in water vapour

As temperature increases, water vapour concentrations in the atmosphere will also increase. Water vapour increases will lead to increases in HO_x and H_2O_2. These changes were discussed in more depth by the Group 1. Their effect on aerosol particles is to increase the oxidation rates of SO_2 and NO_x to form acid precursors both in gas and aqueous phases. An example of this is discussed in the previous section. Dawson *et al*., [2007] conclude that this enhancement in oxidant is most likely to be the main cause of the enhanced sulphur processing observed.

It is expected that ozone concentrations will also change. The increase in water vapour will lead to a decrease in background ozone, whilst increases in regional ozone from pollution plumes are expected to occur. These processes were discussed in more detail in Group 1 but are relevant here as ozonolysis is a main route for the formation of secondary organic aerosol (SOA), though the rates and pathways remain poorly understood at present.

5.3.3 Stability, ventilation and convection

Whilst the IPCC [2007] predicts increases in heat wave events, and at mid latitudes this implies periods of widespread stagnation such as was observed during the European heat wave of 2003, there is little clear evidence to suggest that stagnation events will either increase or decrease in intensity and duration. As was observed during 2003, such events lead to increases in PM above the guideline limit values. There is some evidence to suggest that the frequency of stagnation events decreases during the wintertime. Diurnal temperature variations are predicted to reduce, leading to decreases in nocturnal stability and hence a reduction in aerosol particulate. However, the evidence for the reduction in the diurnal cycle of temperature remains rather weak at present. Convective intensity is predicted to increase substantially in the tropics. This will lead to a reduction PM at the ground as venting will be increased. Given the geographical distribution of the global population is expected to change towards the tropics, this may be an important factor when considering air quality in emerging megacities regardless of climate change influences.

5.3 4 Changes in frequency, distribution and intensity of precipitation

Global average precipitation is predicted to increase in all global climate model predictions of the coming century. As a result the lifetime of aerosols and their precursors with respect to wet deposition will decrease globally. However, regional differences are predicted to occur (Figure 5.4). Given that the global distribution of aerosol particles is not at all homogeneous, the impact on the aerosol burden will be non linear and a function of both changing emission fields and changing precipitation patterns.

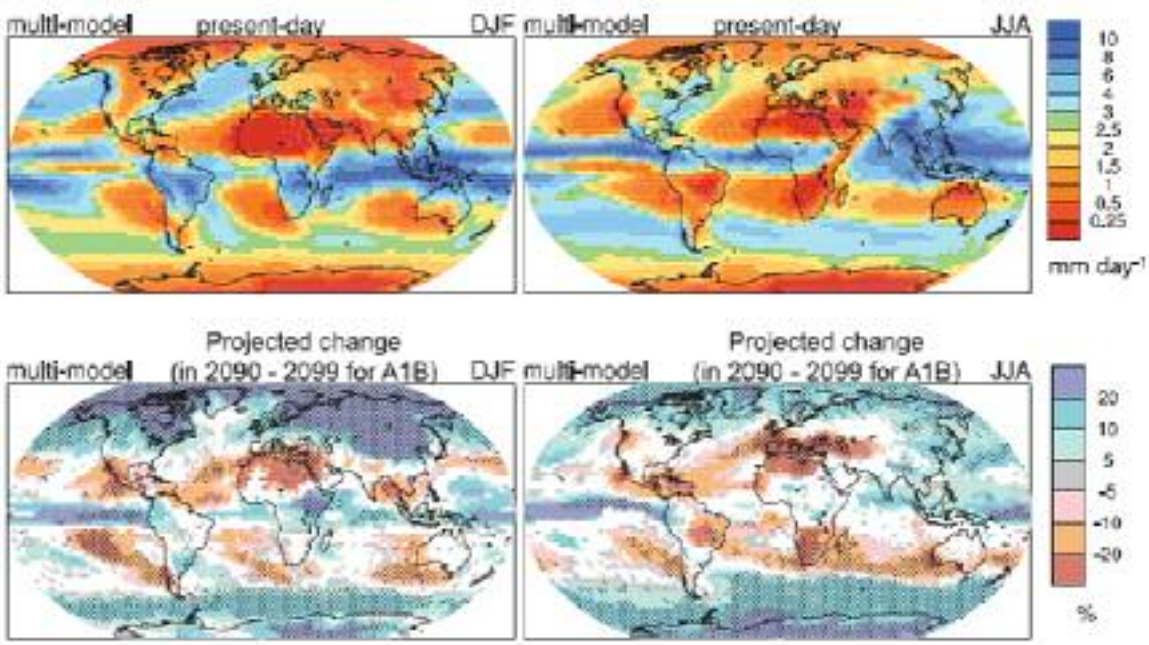


Figure 5,4. Predicted spatial distribution of mean seasonal precipitation for December-January-February (left panel) and June-July-August (right panel) for the period 1979-1993 (top panels) derived from a multiple models using the IPCC A1B emission scenario. The lower panels show the percentage change in precipitation for the period 2090-2099 compared with 1980-1999. No shading is shown unless more than 66 % of the models agree on the sign of the change and the stippling indicates areas where more than 90 % of the models agree on the sign of the change [IPCC 2007].

Northern hemisphere winters show enhanced precipitation at higher latitudes by the end of the century. This is likely to lead to enhancements in wet removal in these locations, although if the precipitation events are more sporadic but intense this may not affect the overall aerosol burden significantly. Conversely, in sub-tropical regions, particularly the Mediterranean but also areas of central America, Australasia, South America, South Africa and southern Asia, projected reductions in precipitation lead to longer lifetimes due to reduced wet removal. Many of these areas are semi-arid and the majority of models predict extended dry periods in these areas. The Mediterranean region and the southern US in particular, are areas of high population. It is expected that these areas will receive higher dust loadings, which are caused by reduced precipitation in regions of already marginal rainfall. This may substantially increase the PM in these regions, not least because dust is predominately larger than 1 μm in diameter and are made of dense material. However, as is discussed in more detail in the by Prospero, section 12, at the present time the links between climate and land use change and dust generation are not clear and conflicting data exist. The air quality problems of dust arising from land use change on regional scales close to large areas of population are largely unrelated to the major, climatically relevant sources of dust and hence, at present these

problems appear to be decoupled. The main dust generation regions are currently not adjacent to major areas of population though this may change in future. More research in this area is necessary.

Decreases in precipitation are likely to lead to longer and more severe drought conditions. This may well lead to an increased frequency of wildfires. When this is coupled with a greater number of people living in such affected areas the risk of wildfires is likely to increases still further. Biomass burning emits substantial concentrations of aerosol, which has been demonstrated to have deleterious effects on human health.

5.3.5 Changes in cloud cover

Cloud cover is predicted to decrease in mid and low latitudes (see Feichter, Figure 1), whilst small increases are predicted at high latitudes. Photochemical production of oxidants in polluted regions is likely to increase if cloud cover decreases as the radiative flux to the surface increases. This will act to increase secondary inorganic aerosol and will have an influence on secondary organic aerosol production but the pathways remain unclear. In addition, increased cover of non precipitating clouds will promote wider scale aqueous processing of aerosols, resulting in an increase in PM. If precipitation occurs, more localised deposition will take place. This is particularly true of sulphate but is far less important for nitrate. The chemical and physical processes affecting inorganic aerosol are relatively well known, however, climate model predictions of cloud cover are at present very rudimentary and this remains a key challenge. In contrast, very little is known about aqueous phase processing of organic material and this is an area of necessary research at the process scale.

5.3.6 Changes in wind speed, gustiness

There is little consensus on changes in wind speed or gustiness from current climate models. The IPCC [2007] report does note that global climate models do forecast increases in storm frequency and intensity over the north Atlantic, central Europe and the southern ocean, though with low predictive skill. Over land areas, dust production may well increase, but so will ventilation. Associated with increased wind speeds, model forecasts also suggest high waves in northern European coastal regions. Given the highly non linear dependence of sea spray production on wind speed [O'Dowd and De Leeuw, 2007], enhancements in high winds close to populated coasts are likely to lead to significant increases in urban and regional PM associated with natural sea spray. Whilst the aerosol is natural, understanding its contribution may well be important when assessing PM impacts close to coasts.

5.4 Essential points and recommendations

At present, the air quality metric used to assess the abundance of particulate matter on air quality is the particulate mass (PM). A large number of aerosol sources contribute to the total PM. Therefore all components of aerosol must, unless proven otherwise, be considered important and should, if possible, be reduced.

Key processes in the lifecycle of certain aerosol components, for example sulphate and nitrate, are reasonably well understood and assessments of changes in their influence on air quality due to climate change are dependent on the ability of regional and global models to capture dynamical and climatic processes on regional scales. However, what is not clear is whether sulphate and nitrate represent part of the toxic fraction of urban PM. Whilst, presently they form part of the aerosol mix that needs to be regulated, it is not clear whether they are part of the toxic fraction or in some way influence it. This is a key issue for air quality and health in the coming years. Nitrate aerosol distribution is

dependent on the free ammonia availability as well as temperature. This needs work to identify current and future nitrate distributions and trends. However, for other components (*e.g.* organics, ultra fine particles and bioaerosols) this is simply not possible as the basic processes are not well enough understood. An understanding of the roles of sulphur and nitrogen in the formation of organic aerosol is needed to establish the effect on SOA of changing NO_x and SO_2 emissions. This is an important topic for the legislator.

Organic aerosol is important as the sources, chemistry, pathways and biogenic/anthropogenic balance will all respond to future changes in climate change. Furthermore, it is an important component of local air quality and regional aerosol, where between 30 to 70 % of submicron PM may be organic in nature [Allan *et al*., 2003; Zhang *et al*., 2005]. Organic aerosol contributes significantly to global submicron aerosol [Kanakidou *et al*., 2005]. Therefore, they present one of the biggest challenges to impacts of climate change on air quality through aerosols

Whilst the current metric is PM; there is growing evidence that ultrafine particles are important from a human health perspective [Donaldson *et al.*, 2006]. Ultrafine particle formation is observed widely in many areas, however, this is very sensitive to changes in ambient conditions and is highly non-linear with temperature.

Better knowledge of cloud and precipitation processes is needed, including the chemical processing organic material. Improved representation of clouds and precipitation processes in global and regional climate models is much needed.

Bioaerosols may well be important sources of ice nuclei and the atmosphere could well be an important pathway for disease and allergen transport via aerosol particles. Little is known about bioaerosols and their behaviour in the atmosphere. However, as biological assay methods improve this is an important area for new research.

Air quality and climate science questions meet on regional scales. It is on these scales that key questions of boundary layer dynamics, convection, and stability and cloud processes and their simulation, including formation, frequency, extent and precipitation, must be better understood. For example processing of aerosols by clouds and wet deposition require accurate prediction of the cloud and precipitation fields not the amounts. This is likely to be an important area of research for some time to come.

References

Allan, J.D., H. Coe, K.N. Bower, P.I. Williams, M.W. Gallagher, M.R. Alfarra, J.L. Jimenez, D.R. Worsnop, J.T. Jayne, M.R. Canagaratna, E. Nemitz, and A.G. McDonald, 2003, Quantitative Sampling Using an Aerodyne Aerosol Mass Spectrometer. Part 2: Measurements of Fine Particulate Chemical Composition in Two UK Cities, *Journal of Geophysical Research – Atmospheres*, Vol. 108, No. D3, 4091, doi:10.1029/2002JD002359.

Dawson, J. P., P. J. Adams, and S. N. Pandis, 2007, Sensitivity of PM2.5 to climate in the Eastern US: a modeling case study, Atmos. Chem. Phys., 7, 4295–4309.

Donaldson, K., 2006, Resolving the nanoparticles paradox, Nanomedicine 1 (2): 229-234.

Heald CL, Jacob DJ, Park RJ, Russell LM, Huebert BJ, Seinfeld JH, Liao H, Weber RJ, 2005, A large organic aerosol source in the free troposphere missing from current models, Geophysical Research Letters 32 (18): Art. No. L18809 SEP 27.

Intergovernmental Panel on Climate Change 2007, (http://www.ipcc.ch/pdf/assessment-report/ar4/wg1)

Kanakidou M, Seinfeld JH, Pandis SN, Barnes I, Dentener FJ, Facchini MC, Van Dingenen R, Ervens B, Nenes A, Nielsen CJ, Swietlicki E, Putaud JP, Balkanski Y, Fuzzi S, Horth J, Moortgat GK, Winterhalter R, Myhre CEL, Tsigaridis K, Vignati E, Stephanou EG, Wilson J Kanakidou M, Seinfeld JH, Pandis SN, Barnes I, Dentener FJ, Facchini MC, Van Dingenen R, Ervens B, Nenes A, Nielsen CJ, Swietlicki E, Putaud JP, Balkanski Y, Fuzzi S, Horth J, Moortgat GK, Winterhalter R, Myhre CEL, Tsigaridis K, Vignati E, Stephanou EG, Wilson J, 2005, Organic aerosol and global climate modelling: a review, *Atmospheric Chemistry and Physics* **5**: 1053-1123.

Kulmala M, Hameri K, Aalto PP, Makela JM, Pirjola L, Nilsson ED, Buzorius G, Rannik U, Dal Maso M, Seidl W, Hoffman T, Janson R, Hansson HC, Viisanen Y, Laaksonen A, O'Dowd CD Overview of the international project on biogenic aerosol formation in the boreal forest (BIOFOR), 2001, *Tellus Series B-Chemical and Physical Meteorology* **53** (4): 324-343.

Morino, Y., Y. Kondo, N. Takegawa, Y. Miyazaki, K. Kita, Y. Komazaki, M. Fukuda, T. Miyakawa, N. Moteki, and D.R. Worsnop, 2006, Partitioning of HNO_3 and Particulate Nitrate Over Tokyo: Effect of Vertical Mixing, *J. Geophys. Res.*, **111**, D15215, doi:10.1029/2005JD006887.

O'Dowd C.D. and De Leeuw G., 2007, Marine aerosol production: a review of the current knowledge, *Philosophical Transactions of the Royal Society* A-Mathematical Physical and Engineering Sciences 365 (1856): 1753-1774.

O'Dowd CD, Hameri K, Makela JM, Pirjola L, Kulmala M, Jennings SG, Berresheim H, Hansson HC, de Leeuw G, Kunz GJ, Allen AG, Hewitt CN, Jackson A, Viisanen Y, Hoffmann T, 2002, A dedicated study of New Particle Formation and Fate in the Coastal Environment (PARFORCE): Overview of objectives and achievements, *Journal of Geophysical Research-Atmospheres* **107** (D19): Art. No. 8108.

Robinson, A.L., Donahue, N.M., Shrivastava, M.K., Weitkamp, E.A., Sage, A.M., Grieshop, A.P., Lane, T.E., Pierce, J.R., Pandis, S.N., 2007, Rethinking Organic Aerosols: Semivolatile Emissions and Photochemical Aging. *Science* 315(5816): 1259-1262. DOI: 10.1126/science.1133061.

Rudich Y, Donahue NM, Mentel TF., 2007, Aging of organic aerosol: Bridging the gap between laboratory and field studies *Annual Review of Physical Chemistry* **58**: 321-352.

Stanier CO, Khlystov AY, Pandis SN, 2004, Ambient aerosol size distributions and number concentrations measured during the Pittsburgh Air Quality Study (PAQS), *Atmospheric Environment* **38** (20): 3275-3284.

World Health Organisation, 2004, United Nations, Department of Economic and Social Affairs Population Division Report ST/ESA/SER.A/236.

Zhang, Q., M.R. Alfarra, D.R. Worsnop, J.D. Allan, H. Coe, M.R. Canagaratna, and J.L. Jimenez, 2005, Deconvolution and Quantification of Hydrocarbon-like and Oxygenated Organic Aerosols Based on Aerosol Mass Spectrometry. *Environmental Science and Technology*, **39:** 4938-4952, doi:10.1021/es048568l.

6. Building observation and modelling systems to cope with the interactions of air quality and climate change

Rapporteur's summary from Group 4

Rapporteur: Laurence Rouil

Institut National de l'Environnement Industriel et des Risques,
F-60550 Verneuil-en-Halatte, France

Group 4 Participants.*Peter Builtjes (Chair), Oystein Hov (Plenary Speaker), Laurence Rouil (Rapporteur), Steffen Beirle, John Burrows, Gitte Hedegaard, Michela Maione, Nicolas Moussiopoulos, Kjetil Torseth, Robert Vautard, Martin Williams*

Plenary Lecture: section 9; participants' contributions, section 13

6.1 Introduction

Links between air quality and atmospheric composition at the ground level on one hand and climate change consequences on the other hand, are now considered as evident issues by both scientists and policy makers. The most visible impact of climate warming in Europe is the increasing ozone background concentrations levels [Meleux *et al*, 2007, Hedegaard, 2007, Hedegaard *et al*, 2007, Langner *et al*, 2005], and consequently an increase of chronic exposure and of the number of days when the health protection thresholds are exceeded. The heat wave that occurred in summer 2003 provides a appropriate example of the adverse heath effects due to the interaction between high temperatures and high ozone levels [Vautard *et al*, 2005, Schär *et al*, 2004]. Changes in atmospheric properties induced by climate warming (water vapour content for instance) also influence air pollutant chemistry and transport. Similarly, radiative forcing from aerosol compounds has an impact on climate, though the positive or negative trends can still be difficult to highlight for some pollutants (Figure 6.1). Anyway, these interactions must be considered when defining emission control policies. Future air quality scenarios cannot be defined in a realistic way, if climate change issues are not considered. The fact is that: 1) the effectiveness of emission control measures can be counterbalanced by increasing temperatures (especially for ozone formation), 2) some climate change and air quality measures may not follow a "win-win" strategy. Diesel engines and wood combustion issues are well-known examples of such conflicting situations. [DEFRA, 2007, Williams, 2007]. Some modelling exercises designed for assessing the potential benefits of a coupled approach to air quality and climate change are thought for policy purposes to be related to the definition of national emission ceilings for the revision of the EU Directive [IIASA, 2006a, 2006b, Dentener *et al,* 2006]. It is expected that such a philosophy will drive the definition of the future regulatory framework as defined in the international protocols and the European directives.

However, if the relevance of linking air quality and climate change control strategies is assumed, the need for building observation and evaluation systems that can deal with both areas arises. *In-situ* networks implemented in Europe allow one to assess the atmospheric composition properties with spatial and temporal coverage that are quite satisfactory, although they could be improved in some locations. Development of earth-observation systems can help overcoming these difficulties, so that the atmospheric composition picture can be improved. Models devoted to air quality and climate analyses are becoming more sophisticated, and scientifically evaluated through dedicated projects. Despite their inherent uncertainties and those due to input data,

model results are considered important enough to be used by policy makers and scientists for understanding current and future situations. So the tools are here, and allowing for their strengths and weaknesses, they are mature enough for promoting an approach that will help building an integrated monitoring system for air quality and climate.

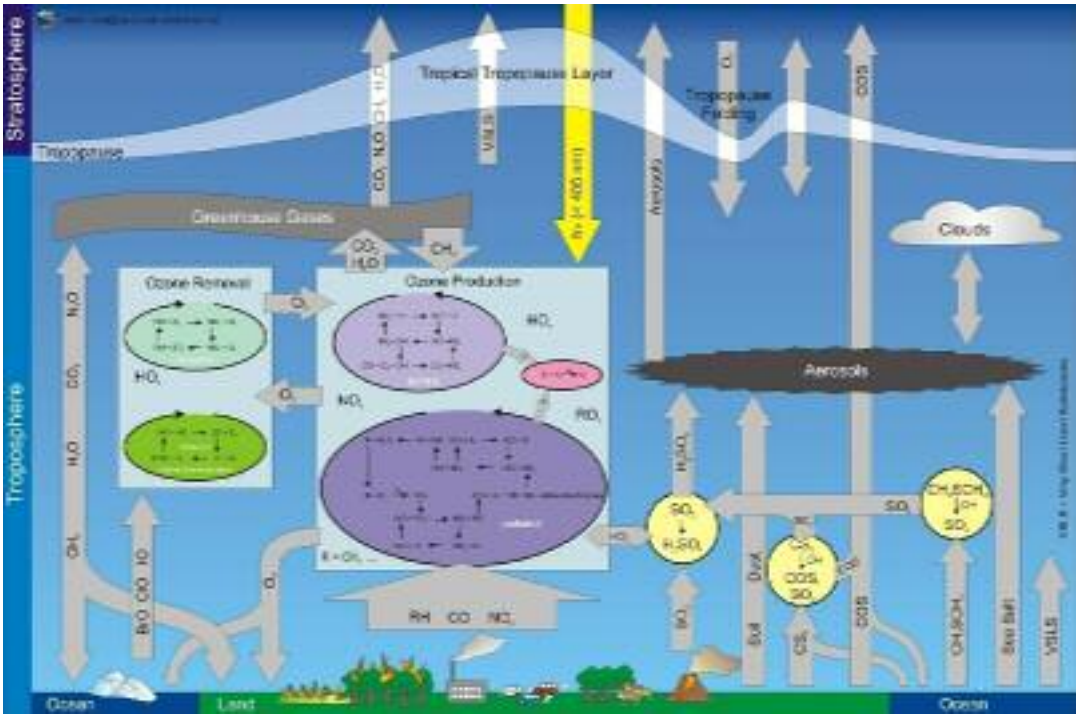


Figure 6.1. Air quality and climate change pollutants interactions

This section aims at reporting recommendations for the implementation of observation and modelling systems that can cope with the interactions of air quality and climate change. The present state has been analysed by the working group, with a special attention dedicated to the identification of gaps, overlaps, and potential synergies. Issues related to *in-situ*, satellite and modelling data have been investigated, and the conclusions are reported in three sections; however, links between the three types of data are discussed in each section. The conclusions emphasise gaps that should be filled in for building monitoring systems integrating all these components.

The species and the parameters that must be monitored are largely known and agreed through previous initiatives : the IGACO review [IGACO, 2004] and the list established in the EMEP monitoring strategy for monitoring transboundary air pollution (*http://www.nilu.no/projects/ccc/reports/Monitoring%20Strategy_full.pdf*) provide basic references. So this point is not discussed further but a brief overview of these variables is given in the annex.

6.2 Recommendations for *in-situ* monitoring networks

The key point is the capacity building challenge of the implementation of relevant observation infrastructures for both air quality and climate, based on existing networks. That means that scientific and structural difficulties need to be overcome.

The most crucial issue is the different levels of development of air quality and climate change monitoring networks. This heterogeneity can be readily explained by the framework supporting such network development.

It is mandatory under the European Framework Directive on Air Quality and its four Daughter Directives[1]. for the EU27 countries to report to the European Commission, air pollutant concentrations of ozone and its volatile organic compounds precursors, nitrogen dioxide, sulfur dioxide, carbon monoxide, benzene, PM_{10}, heavy metals (lead, arsenic, cadmium, mercury) and Polycyclic Aromatic Hydrocarbons.

The Convention on Long Range Transboundary Air Pollution (http://www.unece.org/env/lrtap/welcome.html) requires a European-wide network fit for monitoring air pollutant background concentration and deposition. Pollutants responsible for acidification, eutrophication and ozone ground level concentrations, heavy metals and Persistent Organic Pollutants (POP) are monitored using the EMEP monitoring strategy (www.emep.int). Regulatory reporting allows the assessment of the impact of emission reduction strategies and highlights situations when limit values are exceeded. Regulatory networks are developed, by definition, with a sustainable perspective and designed for providing a realistic picture of air pollution patterns throughout Europe.

In addition, "process-oriented" networks measure the parameters needed for a better understanding of pollutant behaviour and the determinant factors in the occurrence of pollution episodes. These networks can provide chemical and dynamical parameters with a high temporal resolution, and in some cases vertical profiles can even be available. The EUSAAR network of supersites for aerosol properties measurement (www.eusaar.net), the EARLINET lidar network of (www.earlinetasos.org) are well-known examples. Moreover there are some networks devoted to global atmospheric composition that can provide comprehensive information for air quality (see for instance the Bremen DOAS network for atmospheric measurements – BREDOM-http://www.iup.uni-bremen.de/doas/groundbased_data.htm). However they are generally developed and implemented in scientific areas supported by European research projects. So sustainability beyond the project period is not ensured, and data availability for users not directly involved in the project may not be systematic.

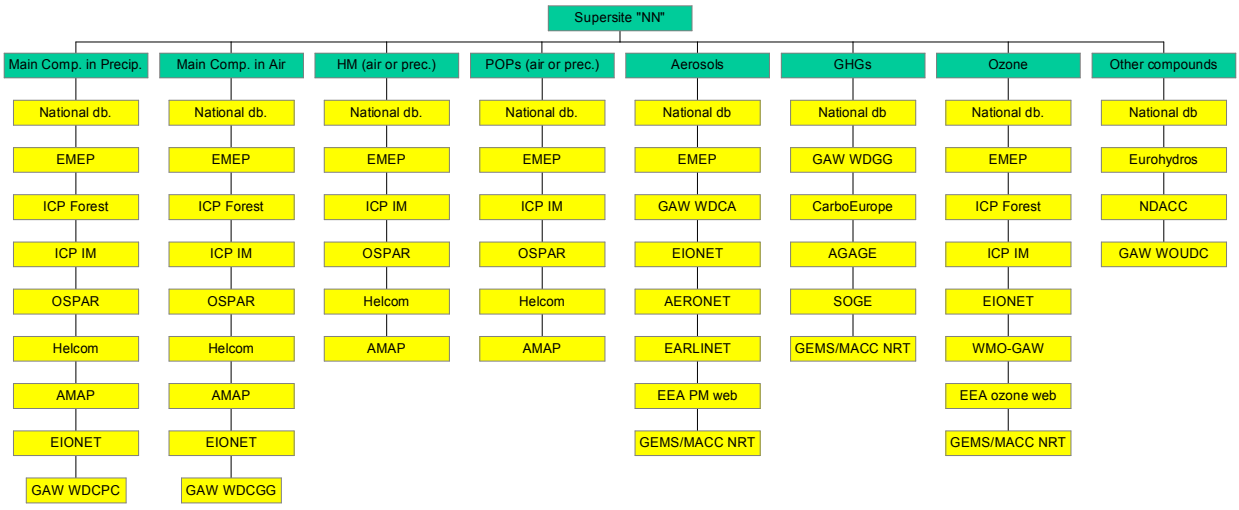


Figure 6.2. International research projects or regulatory programs producing atmospheric data.

So there are numerous air quality monitoring networks in Europe but, unfortunately, they not harmonised either in their methods, or in their geographical coverage. Figure 6.2 gives an overview (established by NILU) of the projects and regulatory

[1] The new Unified air quality directive that should be adopted in spring 2008, will have the same content with reporting of PM2.5 atmospheric concentrations in addition .

frameworks where atmospheric composition data are produced. It demonstrates the wealth of the systems, but also its potential redundancies, and the need for optimisation. However, the development of an integrated approach to measurement and modelling justifies the interest in getting more process-oriented data in an operational way. These data could serve for validation of models as a part of the monitoring system, complementing *in-situ* data.

However for getting consistent data as part of a monitoring network, harmonised measurement methods are needed, especially in the field of aerosol measurement. Methods are now compared for establishing good practice guidelines and references or norms. This is the current priority of the air quality community considering the remarkable results obtained in the EUSAAR project field campaigns (Figure 6.3). These raise new questions related to the difficulty of comparing model results to measurement data. What is the best observation that should be considered for model evaluation?

The last mid-term perspective for air quality in-situ data is the near real time (NRT) reporting. Air quality forecasting and mapping modelling systems are now operational (www.prevair.org, www.eurad.uni-koeln.de) and data assimilation can help improving their performance. That means that observation data must be made available in the few hours following the sample, even if they are not validated. Technical and political questions arise: how to supervise the use of unvalidated data in a wider framework than the scientific ring?

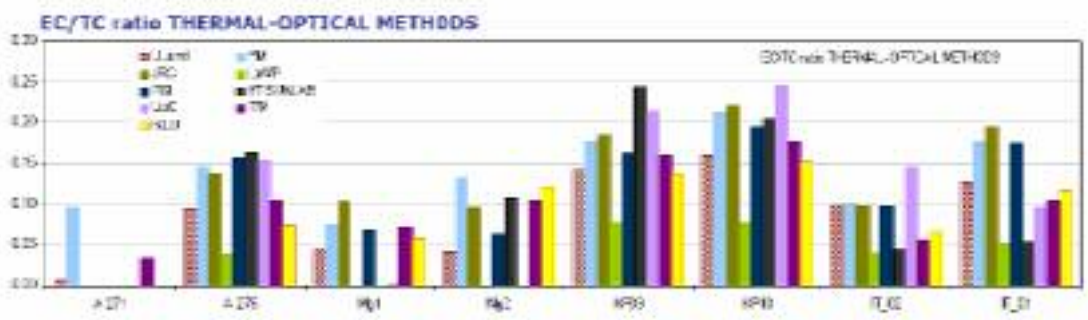


Figure 6.3. Intercomparison of identical filters from several EUSAAR sites operating with similar thermo-optical methods

The situation of climate change monitoring networks is completely different. The main reason is that there is no legal requirement for the species that are concerned (CO_2, methane, halocarbons). The implemented networks result from scientific initiatives (see the ICOS network – Integrated Carbon Observation System - *www.icos-infrastructure.eu* for example), and there is no regulatory mandate to support these infrastructures. Thus, the question of their sustainability is more difficult to solve then for the case of air quality. However the requirements of the international protocols dealing with climate issues, should necessitate the implementation of operational structures monitoring CO_2 and CH_4 fluxes, mixing ratios and dry columns. Admittedly, a few tens of stations correctly spread across Europe should be enough to provide a good representation of pollution patterns and, thanks to inverse modelling, a quantification of the amounts emitted. Monitoring concentrations and emissions with inverse modelling techniques is one of the most interesting developments within climate change monitoring.

This brief summary points out one of the main reason why it is so difficult to establish *in-situ* infrastructures monitoring air quality and climate together. The topics do not have the same development priorities for the short-term. Other reasons worth mentioning: the monitored species are not the same, and the spatial and temporal

resolutions are also different (Figure 6.4). More crucial is the divergence in terms of geographical coverage. Europe is, in our case, the target domain for "regional air quality " purposes, while climate change monitoring leads to world-wide considerations looking for signals in the tropics as well as at other latitudes.

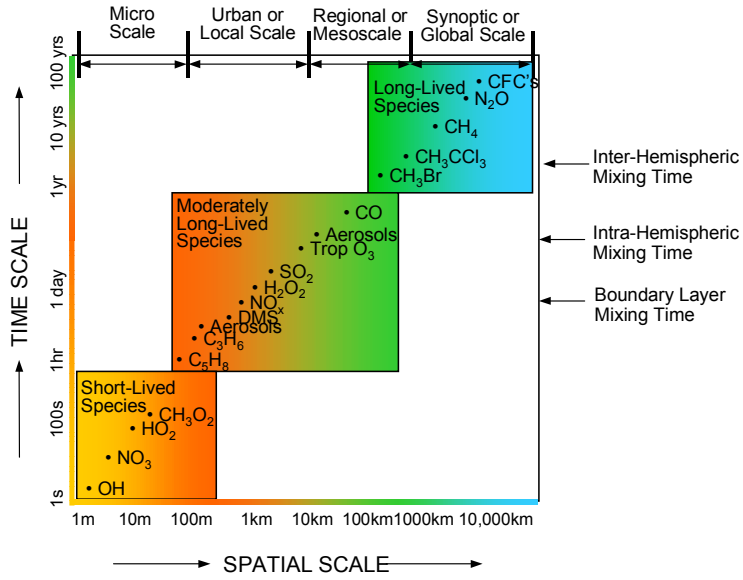


Figure 6.4. Temporal and spatial scales for air quality and climate specific pollutants (image from John Burrows, Bremen).

So there are a number of recommendations to make for promoting the implementation of common air quality and climate change infrastructures.

* Encouraging the current initiatives devoted to a better understanding of the possible links between air quality and climate change and promoting their development. Beyond this objective, they should help to establish common measurement and modelling practices and databases, worthwhile for both communities. This is precisely the stake of the project GEOMON funded by the 6th framework program (www.geomon.eu).

* Informing and involving users, especially policy makers, who could help support the development of operational networks for monitoring climate change species by, perhaps, providing a regulatory framework.

* Developing synergies around a key common issue for air quality and climate: atmospheric aerosols. Better knowledge of aerosol compounds properties is crucial for elaborating relevant control strategies in both fields.

* Enhancing synergies for the measurement of vertical profiles that are sought by air quality and climate change scientists. Lidars, sonde networks could be designed for both, as well as measurement campaigns based on aircrafts and balloon measurements. This would the raising and highlighting of common issues and developing links between the experts and scientists involved.

6.3 Recommendations for satellite data

The situation is rather different when satellite data are considered. History of earth observation, dedicated to the global scale, and also technological considerations have made it easier for climate change purposes. However whichever the field of application, satellite data are essential for filling the vast gaps left by *in-situ* data (in the oceans for instance) and for getting an information about vertical distributions. Satellites offer an

ideal and natural platform for co-located measurements. So some of the recommendations expressed for *in-situ* networks could be easily fulfilled. The key question is how to use satellite data in an operational way for both air quality and climate change monitoring, and how to improve the content of the next space missions for meeting this objective.

The first point that needs to be considered is that measurements must be made faster than the chemical processes that are tracked. And air quality and climate pollutants do not necessarily act on the same spatial and temporal scales (see Figure 6.4). This can be a real constraint for satellite retrievals. As a consequence earth observation, with the current satellites, can only be used for specific applications.

Obviously, analysis of transformation and trends of long-lived species are easier to established then air quality hourly monitoring (Figure 6.5).

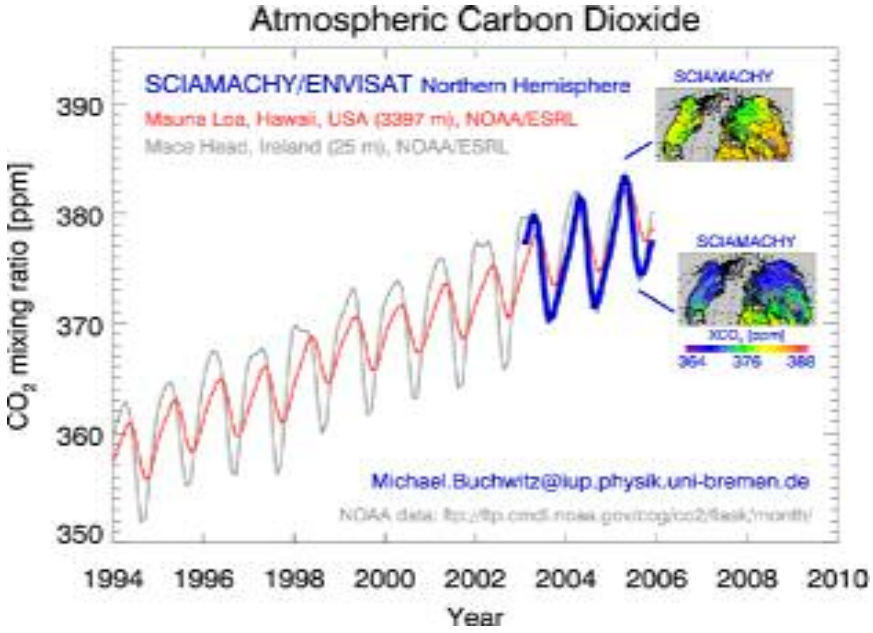
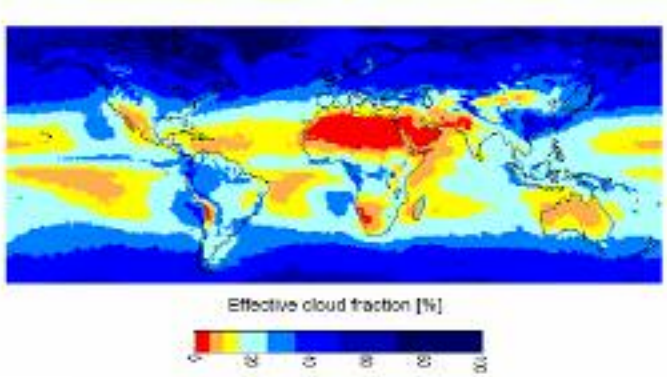


Figure 6.5. CO_2 trends measured by SCIAMACHY

Satellites have the capacity for monitoring climate change feedback on atmospheric parameters [Wagner *et al*, 2006, 2007]: water vapour column, cloud fraction and cloud top height and their links with temperature increase can be studied and trends and correlation can be established (Figure 6.6).

Concerning air quality applications, aerosols, nitrogen dioxide, tropospheric ozone and oxygenated volatile organic compounds (included formaldehyde) can be studied. For these compounds, especially NO_2, some kinds of emission sources can be tracked thanks to the overview from the satellite. Anthropogenic combustion sources such as ship emissions can be qualified and quantified using inverse modelling approaches [Konovalov *et al*, 2006, 2005]. The representation of the impact of natural sources is also one of the main contributions of satellite retrievals: volcanic eruptions (SO_2), desert dust storms (particulate matter) or lightning effects (NO_x) can be isolated for a better understanding of the occurrence of some pollution episodes. Oxygenated volatile organic compounds are not systematically measured by *in-situ* networks, but a better knowledge of the concentration levels found in the atmosphere would be interesting for obtaining new information related to the evolution of biogenic species emissions with climate change.



Fl_ ctive cloud fraction averaged for the period January 1996-December 2002. Please note that snow and ice is also detected as clouds causing high values in polar regions.

Figure 6.6. Cloud fraction (1996-2002) (courtesy of S. Bierle)

The real complementarity between *in-situ* and satellite data should be investigated. Furthermore it could be enhanced through some adjustment of the earth observation strategy.

The recommendations are as follows.

* Implementing a satellite earth-observation infrastructure based on both GEO (geostationary) and LEO (low earth orbit) approaches. The former is required for air quality purposes which require the monitoring of dedicated areas with a high temporal resolution (as *in-situ* supersites). probably one satellite of each type (GEO and LEO) would be enough for Europe, extended to 2 LEO and 3 GEO for the world.
* Improving some instruments such as GOME2, especially in terms of spatial resolution. Currently it is about 80 km × 40 km, and a resolution of 20 km × 20 km can be reached for a better representation of air quality species.
* Filling in the technological gap that should hold from 2012 to 2020 between the ENVISAT and post-Met-Op systems. This is necessary for the improvement of CO_2 and CH_4 global monitoring.
* Promoting integrated coupled approaches by data assimilation with *in-situ* data and models that will allow taking the best benefits from satellite data.

6.4 Recommendations for modelling

Modelling is the essential component of a potential integrated system linking air quality and climate issues. Indeed, only models can display a picture of what may possibly happen in thirty, or fifty years from now or within the next century, although there are always large uncertainties. Further, models can be used to investigate different spatial and temporal scales within nested systems that allow focusing on a given domain taking into account outside contributions through the boundary conditions or the interactions with smaller inside hot spot areas. Meeting these objectives requires one or two-ways nested approaches [Krol *et al*, 2005] that could be important for dealing with both air quality and climate questions. Provided that input data are correctly known and that sufficient computational effort can be made for simulating “real” future climate, it is expected that the impact of climate change on air quality (that means the impact of warmer temperatures, dryer air and higher precipitation levels for instance) can be simulated [see Figure 6.7; Hedegaard, 2007, Hedegaard *et al*, 2007] and [Meleux *et al*, 2007, Szopa *et al*, 2006, Langner *et al* 2005].

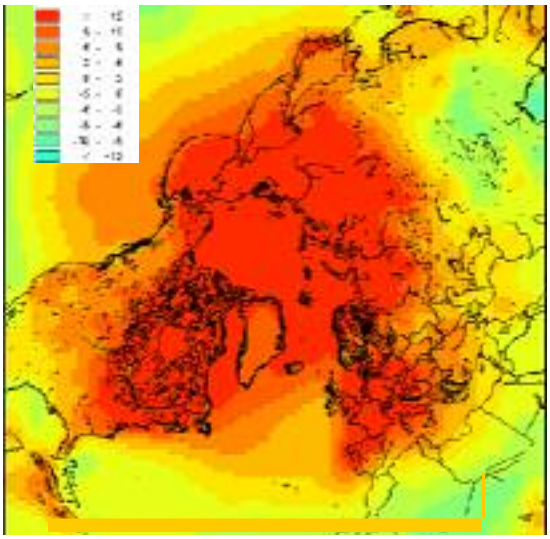


Figure 6.7. Difference in percentage in ozone concentration between the mean values of the two decades 2090s and 1990s. Positive values refers to an increase in the ozone values

Conversely, the impact of air pollutant concentrations on climate change is still a real challenge that is not completely solved. The radiative impact of atmospheric compounds (especially particulates and aerosols) must be quantified and interactions between the atmosphere and the biosphere must be correctly understood. Meeting this challenge also needs an accurate description of the cloud chemistry, which is not at the present time well known. Last but not least, the mutual effects of urban development (and urban air pollution) on climate must be considered, and require new scientific investigations. So current modelling systems can only give a partial view of coupled phenomena. The scientific community is very active in trying to improve the state of the art, and it is expected that future European projects such as those launched within the 7th framework Program will help this cause. The projects CITYZEN (coordinated by the Norwegian Meteorological Institute) and MEGAPOLI (coordinated by the Danish Meteorological Institute) should bring further material (Figure 6.8). This picture also highlights the crucial nodes for uncertainty analysis: emissions and projections, scales bridging, radiative forcing, dynamical and chemical processes.

There are uncertainties at every stage of the modelling approach. Uncertainties in input data (emissions, meteorology, land use, boundary conditions) are more or less correctly identified. There are still large uncertainties in quantifying some anthropogenic emissions (from combustion processes for example) but the main difficulty remains with the biogenic emissions and ecosystem evolutions, that are very sensitive to both air pollution and climate effects [Sanderson *et al*, 2006]. Once more, a lot needs to be done before we can approach multiscale systems with reduced uncertainties. However, integrating *in-situ* and earth observations in models using data assimilation techniques helps to improve some variables, in forest fires emissions for instance [Hodzic *et al*, 2006, 2007]. Uncertainties in meteorological data and boundary conditions, which are always needed in model simulations, can be reduced implementing an ensemble approach combining several model results [Van Loon *et al*, 2006].

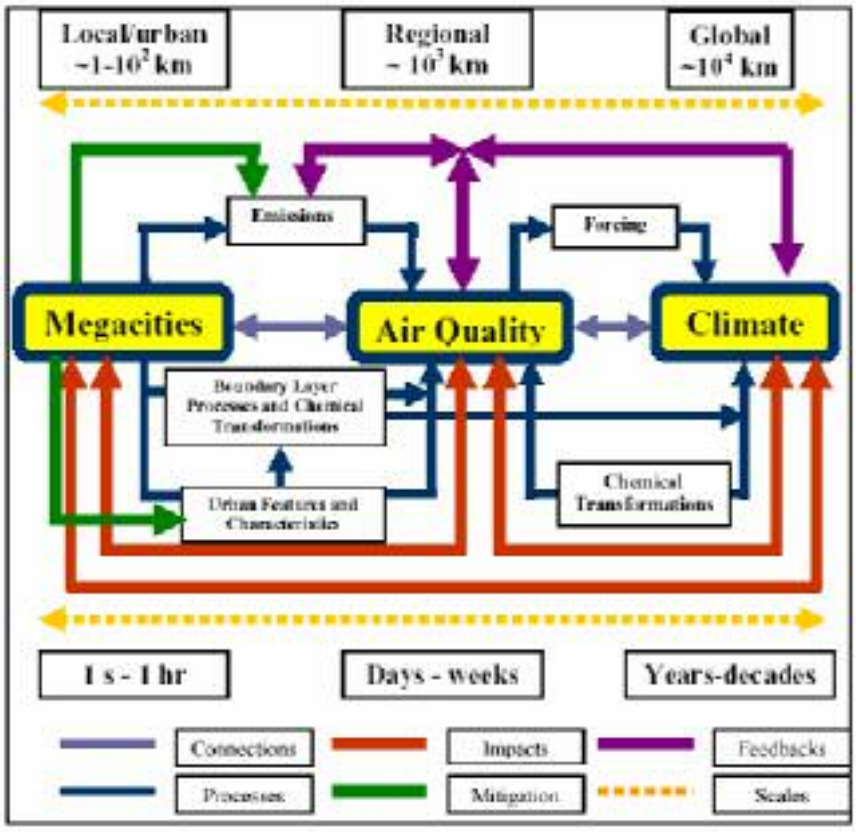


Figure 6.8. Modelling interactions between air quality issued and climate change (from the MEGAPOLI project description)

Uncertainties are also attributed to the model parameterisations themselves. Vertical exchange processes, biogenic emissions, cloud chemistry, radiative properties of the chemical compounds are among the most crucial points, and are considered as priorities for future model developments. Intercomparison model exercises should be promoted for a better understanding of model strengths and weaknesses through an analysis of the range of possible model responses. This is a first step in uncertainty analysis for defining how model improvement should be investigated [Vautard *et al*, 2006]. Model evaluation and benchmarking methodologies should be harmonized. Nowadays such projects result from the initiative of individual groups but there are no reference methods, see Cuvelier *et al,* [2007], the "Ensemble initiative" from the Joint Research Center, *http://ensemble.jrc.it/* and the 'ENSEMBLES' project from EU FP6, *www.ensembles-eu.org*).

Model intercomparison exercises could focus, in a first step, on the summer 2003 period, during the heat wave that concerned most of western Europe. Studying its effects on atmospheric pollutant concentrations should be an excellent approach for establishing the links between air pollution and future climate. The meteorological conditions that occurred during this period are considered as representative of meteorological characteristics in the future decades. So available measurements and simulations related to summer 2003 must be pursued, to enhance our understanding of the links existing between air pollution and climate (see Figure 6.9) [Vautard *et al*, 2007].

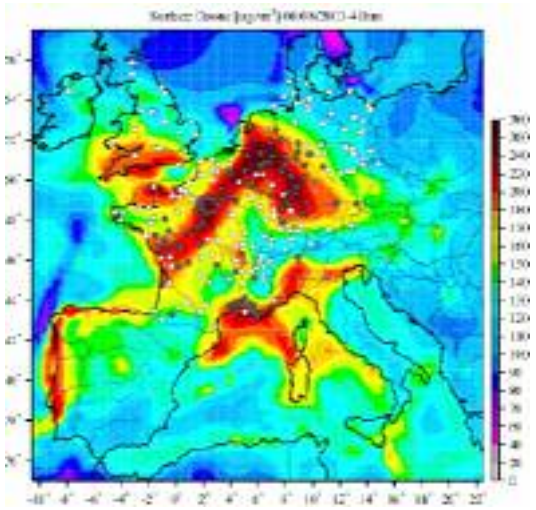


Figure 6.9. Surface ozone concentrations in western Europe during the summer 2003 heat wave (8th August 2003)

Another interest of the modelling approach is the provision of concentration and deposition fields that are useful for analyzing pollution patterns and their origin. Spatialised pollution fields simulated throughout Europe or wider domains can account for observations (both *in-situ* and satellite) implementing data assimilation techniques [Elbern *et al*, 1999, Van Loon *et al*, 2004]. Data assimilation allows us to obtain the most realistic picture of air pollution at given place and time.

Modelling is considered as an important approach for air quality assessment especially if it is combined with measurements. It is also the only available mean for simulating future climate, pollution events and for understanding their relationships. Some recommendations for increasing confidence in modelling for policy making applications are as follows.

* Reducing uncertainties in coupled systems (air quality and climate) with a better description of dynamics and chemical processes (vertical exchange, cloud chemistry, aerosol properties, urban meteorology) ;
* Controlling uncertainties describing input parameters in terms of probability distribution functions ;
* Improving emission description and quantification, especially biogenic emissions that are particularly sensitive to climate change ;
* Developing ensemble systems for focused topics (extreme events for instance) to define the range of possible model responses and assess modelling uncertainties ;
* Promoting integrated approaches linking climate, biosphere and atmosphere systems for a better description of fluxes and concentrations.

6.5 Conclusions

It has been shown in the previous description that tools are available for monitoring climate evolution, air pollutant concentrations and deposition and for forecasting future situation for both issues. Although improvements are still needed to increase their accuracy and to ensure robustness of their results, they are considered as mature enough in each field of application (air quality and climate) for supporting policy makers. However efficient control of both air pollution and climate pollutants will drive future priorities for regulatory purposes. So the development of monitoring and forecasting systems that can account for air quality and climate issues in a coupled manner should

be encouraged. They are necessary for identifying and understanding their reciprocal links for implementing control policies that can deal with both following an optimal approach.

This is the motivation of the recommendations that have been proposed for in-situ and satellite observation systems and for modelling platforms. However implementing monitoring tools and methodologies is not enough. It is also necessary to derive new indicators or metrics that can represent the combined effects of air pollution and climate change. Comparison of global warming potentials of long-lived and short-lived chemical species can be investigated [Boucher *et al*, 2008]. Better qualification and quantification of the effects of atmospheric compounds and integrated systems should help defining the most efficient control policies. Win-win situations (reduction in fuel consumption, new technologies) and trade-off (wood combustion, sulfate emissions) must be highlighted. Their consequences need to be quantified following a common scale of impact that is not defined today, though several instructive analyses have already been done [Williams, 2007, Harmelen *et al*, 2002].

Future monitoring systems that can cope with both air quality and climate issues must also lead to a thorough analysis of the effect of combined control policies. They must support the assessment of the impact of the emission control strategies that are implemented and their improvement. For achieving such an objective, emission projection analysis is a crucial point in this system that undoubtedly needs further development [Cofala *et al*, 2007].

Bridging the available tools, methodologies and input data in the fields of air quality and climate change is the main concern of the scientific and policy making communities. Opportunities exist, and must be explored. Moreover there is a real pressure for elaborating atmospheric emission control strategies that account for high economical constraints that require an optimal choice of the associated measures. In some cases, it is possible that priorities should be defined between air quality and climate. Taking up these challenges will be among the most crucial and interesting ones that the air pollution and climate community will have to deal with in the coming years.

References

Boucher O., Reddy M.S., 2008, Climate trade-off between black carbon and carbon dioxide emissions, *Energy Policy*, **36**, pp 193-200

Cofala J., Amann M., Klimont Z., Kupiainen K., Höglund-Isaksson, 2007, Scenarios of global anthropogenic emissions of air pollutants and methane until 2030, *Atmospheric Environment*, **41**, pp 8486-8499

Cuvelier, C., Thunis, P., Vautard, R., Amann, M., Bessagnet, B., Bedogni, M., Berkowicz, R., Brandt, J., Brocheton, F., Builtjes, P., Coppalle, A., Denby, B., Douros G., Graf, A., Hellmuth, O., Honoré, C., Hodzic, A., Jonson, J., Kerschbaumer, A., de Leeuw, F., Minguzzi, E., Moussiopoulos, N., Pertot, C., Pirovano, G., Rouil, L., Schaap, M., Stern, R., Tarrason, L., Vignati, E., Volta, M., White, L., Wind, P., Zuber, A., 2007: CityDelta: A model intercomparison to explore the impact of emission reductions in 2010 in European cities in 2010, *Atmospheric Environment*, **41**, 189-207.

DEFRA, 2007, Air quality and climate change : a UK perspective, DEFRA report, www.defra.gov.uk/environment/airquality

Dentener F., D. Stevenson, K. Ellingsen, T. van Noije, M. Schultz, M. Amann, C. Atherton, N. Bell, D. Bergmann, I. Bey, L. Bouwman, T. Butler, J. Cofala, B. Collins, J. Drevet, R. Doherty, B. Eickhout, H. Eskes, A. Fiore, M. Gauss, D. Hauglustaine, L. Horowitz, I. S. A. Isaksen, B. Josse, M. Lawrence, M. Krol, J. F. Lamarque, V. Montanaro, J. F. Müller, V. H. Peuch, G. Pitari, J. Pyle, S. Rast, J. Rodriguez, M. Sanderson, N. H. Savage, D. Shindell, S. Strahan, S. Szopa, K. Sudo, R. Van Dingenen, O. Wild, and G. Zeng, 2006, The Global Atmospheric Environment for the Next Generation, *Environmental Sciences and technologies*, **40**, N°11, pp 3586-3594.

Elbern H. et Schmidt H., 1999, A four-dimensional variational chemistry data assimilation scheme for Eulerian chemistry transport modelling, *Journal of Geophysical Research*, **104**, pp 18583-18598

Hedegaard, G. B., 2007, Impacts of climate change on air pollution levels in the Northern Hemisphere, *NERI Technical Report,* 240, National Environmental Research Institute, University of Aarhus, pp. 107. http://www2.dmu.dk/Pub/AR240.pdf

Hedegaard, G. B., J. Brandt, J. H. Christensen, L. M. Frohn, C. Geels, K. M. Hansen and M. Stendel, 2007, Impacts of climate change on air pollution levels in the Northern Hemisphere with special focus on Europe and the Arctic, *Atmospheric Chemistry and Physics Discussion*, in press

Hozdic A., Vautard R., Chepfer H., Goloub P. et al, Evolution of the aerosol optical thickness over Europe during the August 2003 heat wave as seen from POLDER data and CHIMERE model simulations, 2006, *Atmospheric Chemistry and Physics,* **6**, pp 1853-1864

Hozdic A., Madronich S., Bohn B., Massie S., Menut L., Wiedinmyer C., 2007, Wildfire particulate matter in Europe during summer 2003: meso-scale modelling of smoke emissions, transport and radiative effects, *Atmospheric Chemistry and Physics Discussions*, **7**, pp 4705-4760

IGACO, 2004, the changing atmosphere, an integrated global atmospheric chemistry observation theme for IGOS partnership, *Report GAW n°159,* WMO TD n°1235

IIASA, 2006a, Cost-effective Emission Reductions to meet the Environmental Targets of the Thematic Strategy on Air Pollution under Different Greenhouse Gas Constraints*, NEC Scenario Analysis Report Nr. 5* , http://www.iiasa.ac.at/rains/index.html

IIASA, 2006b, Updated Baseline Projections for the Revision of the Emission Ceilings Directive of the European Union *, NEC Scenario Analysis Report Nr. 4*, http://www.iiasa.ac.at/rains/index.html

Konovalov I. B., Beekmann M., Richter A., and Burrows J. P., 2006, Inverse modelling of the spatial distribution of NOx emissions on a continental scale using satellite data, *Atmospheric Chemistry and Physics*, **6**, pp 1747-1770

Konovalov I. B., Beekmann M., Vautard R, Burrows J.P., Richter A., Nüß H., and Elansky N., 2005, Comparison and evaluation of modelled and GOME measurement derived tropospheric NO2 columns over Western and Eastern Europe, *Atmospheric Chemistry and Physics*, **5**, pp 169- 190

Krol M., Houweling S., Bregman B. , Van den Broek M. , Segers A., Van Velthoven P., Peters W., Dentener F.and Bergamaschi P. , 2005, The two-way nested global chemistry-transport zoom model TM5: algorithm and applications, *Atmospheric Chemistry and Physics*, **5**, pp 417-432

Langner J., bergström R., Foltescu V., 2005, Impact of climate change on surface ozone and deposition of sulphur and nitrogen in Europe, *Atmospheric Environment,* **39***,* Issue 6, Pages 1129-1141

Meleux F., Solmon F., Giorgi, F., 2007, Increase in summer European ozone amounts due to climate change, *Atmospheric Environment*, **41**, 35, 7577-7587

Sanderson M.G., Collins W.J., Johnson C.E., Derwent R.G., 2006, Present and future acid deposition to ecosystems : the effect of climate change, *Atmospheric Environment*, **40**, 1275-1283

Schär, C., Vidal, P. L., Lüthi, D., Frei, C., Häberli, C., Liniger, M. A., and C. Appenzeller, 2004, The role of increasing temperature variability in European summer heatwaves, *Nature* **427**, 332-336.

Szopa, S., Hauglustaine, D. A., Vautard, R., Menut, L., 2006 : Future global tropospheric ozone changes and impact on European air quality. *Geophys. Res. Lett.*, **33**, L14805, doi:10.1029/2006GL025860.

Van Harmelen T., Bakker J., De Vries B., Van Vuuren D., Den Elzen M., Mayerhofer P., 2002, Long-term reductions in costs of controlling regional air pollution in Europe due to climate policy, *Environmental Science and Policy*, **5**, 349-365

Van Loon, M., R. Vautard, M. Schaap, R. Bergström, B. Bessagnet, J. Brandt, P.J.H. Builtjes, J. H. Christensen, K. Cuvelier, A. Graf, J.E. Jonson, M. Krol, J. Langner, P. Roberts, L. Rouil, R. Stern, L. Tarrasón, P. Thunis, E. Vignati, L. White, P. Wind, 2007: Evaluation of long-term ozone simulations from seven regional air quality models and their ensemble average. *Atmospheric. Environment*, **41**, 2083-2097.

Van Loon M., Builtjes P.J.H., Segers A.J., 2004, Modelling and data assimilation of ozone*, Air pollution modelling and its application XIV*, Ed. Springer US.

Vautard, R., Honoré, C., Beekmann, M. and L. Rouil, 2005: Simulation of ozone during the August 2003 heat wave and emission control scenarios. *Atmospheric Environment,* **39**, 2957-2967.

Vautard, R., M. Van Loon, M. Schaap, R. Bergström, B. Bessagnet, J. Brandt, P.J.H. Builtjes, J. H. Christensen, K. Cuvelier, A. Graf, J.E. Jonson, M. Krol, J. Langner, P. Roberts, L. Rouil, R. Stern, L. Tarrasón, P. Thunis, E. Vignati, L. White, P. Wind, 2006a: Is regional air quality model diversity representative of uncertainty for ozone simulation ? *Geophys. Res. Lett.*, **33**, L24818, doi:10.1029/2006GL027610.

Vautard, R., M. Beekmann, J. Desplats, A. Hodzic, S. Morel, 2007. Air quality in Europe during the summer of 2003: a prototype of air quality in a warmer climate. *CR Geoscience*, **339**, pp 747-763

Wagner, T., S. Beirle, M. Grzegorski, U. Platt, 2006, Global trends (1996 to 2003) of total column precipitable water their relation to surface-near temperature, *Journal of Geophysical Research* (to be completed)

Wagner, T., S. Beirle, M. Grzegorski, U. Platt, Dependence of cloud fraction and cloud top height on surface temperature, submitted to ACPD

Williams M. 2007, UK air quality in 2050- synergies with climate change policies*, Environmental Science and policy*, **10**, 169-175

oOo

Annex 1: Overview of the pollutants and atmospheric parameters that should be documented by an integrated system monitoring air quality and climate

Atmospheric constituents:

ozone (O_3)
carbon monoxide (CO)
chlorine monoxide (ClO)
CFC-12 (CF_2Cl_2)
methane (CH_4)
sulfur dioxide (SO_2)
nitrogen monoxide (NO)
water vapour (H_2O)
nitrogen dioxide (NO_2)
hydrogen chloride (HCl)
HCFC-22 ($CHClF_3$)
formaldehyde (HCHO)
nitric acid (HNO_3)
methyl bromide (CH_3Br)
carbon dioxide (CO_2)
bromine oxide (BrO)
nitrous oxide (N_2O)
chlorine nitrate ($ClONO_2$)
volatile organic compounds (VOC)
chlorine dioxide (OClO)
halons (*e.g.* CF_3Br)

Atmospheric parameters:

$J(NO_2)$ and $J(O^1D)$ (UV radiation at specific wavelengths in the troposphere).
and the following aerosol optical properties at multiple wavelengths:
optical depth (*VIS*+*IR*) extinction coefficient (*VIS*) absorption optical depth (*VIS*)
temperature (T)
cloud-top height
solar radiation
pressure (p)
cloud coverage
lightning flash frequency
fire frequency
albedo
wind (u, v,w)

Annexe 2. Table from the **EMEP MONITORING STRATEGY AND MEASUREMENT PROGRAMME 2004-2009**

http://www.nilu.no/projects/ccc/reports/Monitoring%20Strategy_full.pdf

Table Monitoring requirements for the various levels specified by the EMEP monitoring strategy. (Mandatory level 1 and level 2, with compliance according to paras. 20 and 21)

Programme	Parameters	Minimum time resolution	Reference methodology [1]	Notes
Level-1 sites:				
Inorganic compounds in precipitation	$SO_4^{=}$, NO_3^-, NH_4^+, H^+ (pH), Na^+, K^+, Ca^{++}, Mg^{++}, Cl^- (cond)	24hr-Daily	Wet-only/bulk IC/AES/AAS	
Heavy metals in precipitation	Cd, Pb (1st priority), Cu, Zn, As, Cr, Ni (2nd priority)	Daily/weekly	Wet-only/bulk ICP MS or GF-AAS	
Inorganic compounds in air	SO_2, $SO_4^{=}$, NO_3^-, HNO_3, NH_4^+, NH_3, (sNO_3, sNH_4), HCl,Na^+, K^+, Ca^{++}, Mg^{++}	24hr-Daily	FP-filter pack IC/AES/AAS	Needs to be complemented with low-cost denuders
NO_2 in air	NO_2	24hr-Daily	Nal method	Continuous NOx monitors with photolytic converter may be used
Ozone in air	O_3	Hourly	UV-abs	
PM mass in air	$PM_{2.5}$, PM_{10}	Hourly/Daily	LVS-PM_{10} HVS-PM_{10} or equivalent	Gravimetric methods preferred, but monitors can be used where equivalence can be demonstrated.
Gas particle ratios	NH_3, NH_4^+,HCl HNO_3, NO_3^- (in combination with filter pack sampling)	Monthly	Low cost Denuder	Low-cost alternative to basic PM speciation that provides necessary gas-particle ratios for level-1 sites.
Meteorology	Precipitation amount (RR), temperature (T), wind direction (dd), wind speed (ff), relative humidity (rh), atmospheric pressure (pr)	Hourly	AWS	Can be taken from a representative meteorological site
Level-2 sites (additional parameters)		*Level-2 sites should also measure all parameters required at level 1*		
Acidification and eutrophication				
Gas particle ratio	NH_3/NH_4^+, HNO_3/NO_3^- (artifact-free methods, contribute also to PM)	Hourly/Daily	Manual denuders	Continuous denuders/steam-jet may also be used. Replace low cost denuders from level 1. See also PM speciation.
Ammonia in emission areas (optional)	NH_3	Monthly	Low cost denuders	Optional low-cost alternative to provide high spatial resolution information in emission areas, where desired.
Photochemical oxidants				
NOx	NO, NO_2	Hourly	Monitor	NOx monitors with photolytic converter
Light hydrocarbons	C_2-C_7	Hourly	Monitor or canister/GC	Monitoring 10-15 min twice a week may also be used
Carbonyls	Aldehydes and ketones	3hourly twice a week	2,4 DNPH silica cartridges/ HPLC	
Heavy metals				
Mercury in precipitation	Hg	Weekly	Wet-only/bulk CV-AFS	Spec. sampling of borosilicate or halocarbon
Mercury in air	Hg (total gaseous mercury)	Hourly/Daily	Monitor or gold traps CV-AFS	Sampling 1 day per week (or weekly)
Heavy metals in air	Cd, Pb (1st priority), Cu, Zn, As, Cr, Ni (2nd priority)	Daily/Weekly	HVS or LVS/ICP MS or GF-AAS	Analytical method is determined by the concentration level
Persistent organic pollutants				
POPs in precipitation	PAHs, PCBs, HCB, chlordane, HCHs, DDT/DDE	Weekly	Wet-only/bulk GC-MS/HPLC	
POPs in air	PAHs, PCBs, HCB, chlordane, HCHs, DDT/DDE	Daily/Weekly	HVS, PUF foam GC-MS/HPLC	Sampling 1 day per week (or weekly)
Particulate matter				
Major inorganics in both $PM_{2.5}$ and PM_{10}	$SO_4^{=}$, NO_3^-, NH_4^+, Na^+, K^+, Ca^{++}, Mg^+ (Cl^-)	Hourly/Daily	Manual denuders or continuous monitors	Continuous denuder/steam-jet and other instruments may also be used
Mineral dust in PM_{10}	Si	Daily/Weekly	XRF, INAA, PIXE	Reference methodology is under development
Elemental carbon (EC) Organic carbon (OC)	EC, OC	Daily/Weekly	Thermooptical	

Table (cont.) Monitoring requirements for the various levels specified by the EMEP monitoring strategy. (Monitoring at level 3 is research-based and voluntary)

Programme	Parameters	Minimum time resolution	Reference methods[1]	Notes
Level-3 sites: (monitoring at these sites does not require all level 1 and level-2 parameters)				
Dry deposition flux of sulphur and nitrogen species	SO_2, NH_3, HNO_3 ($SO_4^{=}$, NH_4^{+}, NO_3^{-})	Hourly/Daily	-	Contributes to acidification and eutrophication EMEP programme for evaluation of effects on ecosystems and health
Dry deposition flux of O_3	O_3	Hourly/Daily	-	Contributes to photo-oxidant EMEP programme for evaluation of effects on ecosystems and health.
Hydrocarbons	C_2-C_{12}	Hourly/Daily	-	Contributes to photo-oxidant EMEP programme for evaluation of effects on ecosystems and health.
NOy chemistry	NO, NO_2, PAN, organic nitrates	Hourly/Daily	-	Contributes to photo-oxidant and particulate matter EMEP programmes for evaluation of effects on ecosystems and health.
OC speciation	Both water soluble and water insoluble OC	Hourly/Daily	-	Contributes to EMEP programme for PM evaluation of effects on health and analysis of synergies with global change
"Black carbon"	BC	Hourly/Daily	-	Contributes to EMEP programme for PM evaluation of effects on health and analysis of synergies with global change
Size/number distribution	dN/dlogDp	Hourly/Daily	-	Contributes to EMEP programme for PM evaluation of effects on health and analysis of synergies with global change
Light scattering	Aerosol optical depth	Hourly/Daily	-	Contributes to EMEP programme for PM evaluation of effects on health and analysis of synergies with global change
Vertical profiles	O_3 soundings, PM lidar	Hourly/Daily	-	Contributes to EMEP modelling of intercontinental pollution transport
Mercury speciation	TGM, RGM and TPM	Daily/Weekly	-	Contributes to EMEP programme on heavy metals for evaluation of effects on ecosystems and health.
Congener-specific	POPs: PCBs, PAHs, PCDDs and PCDFs	Daily/Weekly	-	Contributes to EMEP programme on POPs for evaluation of effects on ecosystem and health.
Multi-compartment (air, soil, water)	POPs and Hg	Daily/Weekly	-	Contributes to EMEP programme on heavy metal and POPs for evaluation of effects on ecosystems and health.

1) Reference methods can change in time as new methods become available. AAS: Atomic Absorption Spectroscopy; CV-AFS: Cold Vapour Atomic Fluorescence Spectroscopy; GF-AAS: Graphite Furnace Atomic Absorption Spectroscopy; DNFH: Dinitrophenylhydrazin; FP: Filter Pack; PUR: Polyurethane, GC: Gas Chromatography; HPLC: High Performance Liquid Chromatography; HVS: High Volume Samples; LVS: Low Volume Samples; ICP-MS: Inductively Coupled Plasma Mass Spectrometry; PIXE: Proton Induced X-ray Emission; INAA: Neutron Activation Analysis; XRF: X-ray Fluorescence; IC: Ion Chromatography; AES: Atomic Emission Spectroscopy, GC-MS: Gas Chromatography- Mass Spectroscopy. AWS: Automatic Weather Station.

7. Conclusions and recommendations

Each of the four groups provided arguments and recommendation for future research. The following is an edited version of the recommendations.

7.1 Investigating changes in photo-oxidants, precursors and feedback mechanisms

7.1.1 Emissions

* Scenarios should be developed which not only take into account actual and direct future anthropogenic and biogenic emissions but which also try to implement downstream human-induced changes related to emission control and land-use change.
* *In situ* and remote measurement techniques for the analysis of the whole range of biogenic VOCs (*i.e.* isoprene, monoterpenes, sesquiterpenes) should be developed in order to give a longer term perspective on change in the oxidative environment.
* Emission inventories for biogenic VOCs should be improved both on the spatial and temporal scale and be expanded to include speciated terpenoids of higher carbon number.
* Usage of satellites to assess both natural and biogenic emissions of VOCs (*e.g. via* oxidation products) should be seen as a key tool in detecting directly climate induced responses with influence on photo-oxidants.
* Potential emissions in hitherto remote regions, for example new shipping routes in the Arctic ("North-West Passage") should be explored and their long-range impact on the European and US boundary-layer concentrations should be fully explored.
* Usage of *in situ* and remote measurements to observe land-use change related to a warmer climate (due to natural processes and anthropogenic activities (bio fuel production/sequestration) should be integrated fully with biogenic emissions inventories.

7.1.2 Chemical Processes

* Continuous measurements of tracer compounds should be used for determination of changes related to the long term trends in reactivity of the atmosphere by *in situ* and remote techniques. Potential candidates are:
    - peroxides and their precursors
    - HCHO
    - PAN
    - organic nitrates
    - oxygenated VOCs
* Development of improved structure activity relationship (SARs), to model degradation pathways and reactivities especially for the higher molecular biogenic compounds, such as terpenes and sesquiterpenes are required.
* Development and validation of Arrhenius expressions for rate constants over wider temperature ranges than at present is needed.
* Investigation of reaction rates of $RONO_2$ (organic nitrates) with higher carbon number.
* Investigation of exact reaction pathways of alkoxy radicals (isomerisation/degradation).

* Development of atmospheric chemistry models (regional and global) capable of handling reactions at increased temperatures, say up to 40 ^{o}C.

7.1.3 Dynamics

* Combination of satellite and ground-based observations to detect changes in dynamic processes in the atmosphere.
* The use of explicit models to explain and forecast air pollution issues, rather than adapting numerical weather forecast models for this purpose.
* Knowledge of the vertical distribution of air pollutants and information on boundaries between different lower layers of the atmosphere and exchange processes should be improved.
* The use of continuous vertical observation platforms should be enforced and extended to reactive photochemical species. Examples are: long-term aircraft campaigns (*e.g.* CARIBIC), balloon soundings, zeppelins, and the use of high-tower networks.

7.1.4 General

Heat wave events, such as those experienced in Europe in 2003, can be important in guiding our thinking and understanding of photochemistry in future climates (Schar *et al*., 2004). Observations in such events are limited to only those made continuously and those where there is serendipitous coincidence of short-term activity with extreme event.

* The European capacity to undertake responsive and short-term detailed observation and modelling campaigns of extreme pollution episodes should be enhanced.

7.2 Investigating changes in surface-atmosphere interactions

7.2.1 Oceans and ice

* To better predict the impact of climate change on polar and especially Arctic air quality, improved modelling of sea ice dynamics is required. Measurement campaigns and a continuous monitoring of surface halogen and O_3 concentrations are recommended to complement satellite data.

7.2.2 Soils

* Future research should address extreme events that are likely to affect soil water content significantly such as floods and droughts, as these are predicted to occur more frequently.
* Freeze-thaw events are known to trigger spring-time N_2O emission pulses, and as permafrost recedes there is likelihood that wider areas will be affected by this phenomenon, warranting further studies.
* More field data are needed to demonstrate whether wetland CH_4 emissions are already responding to climate change, and more generally the global CH_4 budget should be better understood and quantified.
* Integrated research efforts should bring together different scientific communities and projects that are currently focusing, with too little interaction, on fields as wide-ranging as satellite data, remote sensing and process understanding.

7.2.3 Vegetation

* Since major global change factors such as CO_2, O_3, drought and temperature are known to influence the biogenic source strength of VOCs, the short- and long-term responses of VOC emissions to each factor and to their combinations are required as a priority.

* To better quantify national and global source strengths of VOCs at present and in future, it is crucial to develop spatially resolved vegetation/land-use and speciation maps at different spatial scales, forming a reliable basis to assess future projected changes. Spatially and temporally disaggregated hydrometeorological data are also needed to quantify biogenic emissions.

* An improved understanding of species specific compensation points in vegetation for NH_3 and oxygenated VOCs for dominant plant species and land management in the model domain is necessary. Coupled predictive meteorological -VOC emission - air chemistry - transport models should be developed for studying the impact of biogenic sources on air quality, incorporating biogenic processes on shorter timescales, for application on small as well as larger spatial scales.

* For the assessment of ozone damage to vegetation, and feedback effects on trace gas exchange, there clearly is a need to develop a new assessment tool based on ozone uptake by plants, rather than the currently used AOT40 exposure approach.

7.2.4 Land use changes: biomass burning, urbanization, agriculture

* The response of biomass burning to climate change needs to be quantified. Research is needed on the net climatic and air quality impacts of biofuel production and use within the framework of integrated studies.

* As major land use changes are expected in the tropics, current and future trends of biogenic VOC emissions from tropics and their speciation should be assessed. In all these research areas, improved land use datasets (finer spatial resolution, better speciation) are required both for present conditions and projected changes.

* As megacities develop and since current global estimates of anthropogenic VOC emissions are based on data from very few selected countries from the northern hemisphere, speciated anthropogenic VOC emissions globally need to be quantified at different spatial scales, more particularly in developing countries.

7.2.5 Atmospheric processes: turbulence, energy partitioning, hydrometeorology

* At present the consensus on effects of climate change on the frequency of summer-time air quality episodes is that the frequency will increase, but there are many uncertainties, and studies to tackle this issue need to integrate many of the aspects, including increased urbanization to agricultural land use changes, and the need for speciated anthropogenic and biogenic VOCs data to coupled meteorological-emission-chemistry-transport models. At the ecosystem level, a better understanding of chemical reactions on vegetation surfaces and inside the canopy air space is needed.

7.3 Investigating changes in aerosols and their precursors

Air quality and climate science questions meet on regional scales, and it is on these scales that key questions of boundary layer dynamics, convection, and stability and cloud processes and their simulation, including formation, frequency, extent and precipitation, must be better understood. For example processing of

aerosols by clouds and wet deposition requires accurate prediction of the cloud and precipitation frequency and amount.

7.3.1 Inorganic aerosol

* Work is needed on to identify current and future trends in nitrate aerosol distributions which depend on the free ammonia availability as well as temperature.

* An improved understanding of the roles of sulphur and nitrogen in the formation of organic aerosol is needed to establish the effect on SOA of changing NO_x and SO_2 emissions. This is an important topic for the legislator.

7.3.2 Organic aerosol

* Organic aerosol is important as the sources, chemistry, pathways and biogenic/anthropogenic balance will all respond to future changes in climate change. Furthermore, it is an important component of local air quality and regional aerosol, where between 30-70 % of submicron PM may be organic in nature. Therefore, they present one of the biggest challenges to impacts of climate change on air quality through aerosols. Considering the many uncertainties in the understanding, and the likely increase with climate change, much work is required to elucidate the fundamental processes involved in the formation, processing and precipitation of organic aerosols.

7.2.3 Ultrafine particles

* Whilst the current metric is PM; there is growing evidence that ultrafine particles are important from a human health perspective [Donaldson *et al.*, 2006]. Ultrafine particle formation is observed widely in many areas, however, this is very sensitive to changes in ambient conditions and is highly non linear with temperature. Considering the potential effects of ultrafine particles on human health, detailed work is needed on their formation and processing.

7.2.4 Aerosols and clouds

* Improved representation of clouds and precipitation processes in global and regional climate models is much needed as well as a better knowledge of aerosol cycling due to cloud and precipitation processes.

7.2.5 Bioaerosols

* Bioaerosols may well be important sources of ice nuclei and the atmosphere could well be an important pathway for disease and allergen transport via aerosol particles. Little is known about bioaerosols and their behaviour in the atmosphere. However, as biological assay methods improve this will be an important area for needed research.

7.4 Building observation and modelling systems to cope with future change

7.4.1 In-situ monitoring

So there are a number of recommendations to make for promoting the implementation of common air quality and climate change infrastructures.

* Encouraging the current initiatives devoted to a better understanding of the possible links between air quality and climate change and promoting their development. Beyond this objective, they should help to establish common measurement and modelling practices and databases, worthwhile for both communities. This is precisely the stake of the project GEOMON funded by the 6^{th} framework program (*www.geomon.eu*).

* Informing and involving users, especially policy makers, who could help support the development of operational networks for monitoring climate change species by, perhaps, providing a regulatory framework.
* Developing synergies around a key common issue for air quality and climate: atmospheric aerosols. Better knowledge of aerosol compounds properties is crucial for elaborating relevant control strategies in both fields.
* Enhancing synergies for the measurement of vertical profiles that are sought by air quality and climate change scientists. Lidars, sonde networks could be designed for both, as well as measurement campaigns based on aircrafts and balloon measurements. This would the raising and highlighting of common issues and developing links between the experts and scientists involved.

7.4.2 Satellite data

The recommendations are as follows.

* Implementing a satellite earth-observation infrastructure based on both GEO (geostationary) and LEO (low earth orbit) approaches. The former is required for air quality purposes which require the monitoring of dedicated areas with a high temporal resolution (as *in-situ* supersites). probably one satellite of each type (GEO and LEO) would be enough for Europe, extended to 2 LEO and 3 GEO for the world.
* Improving some instruments such as GOME2, especially in terms of spatial resolution. Currently it is about 80 km × 40 km, and a resolution of 20 km × 20 km can be reached for a better representation of air quality species.
* Filling in the technological gap that should hold from 2012 to 2020 between the ENVISAT and post-Met-Op systems. This is necessary for the improvement of CO_2 and CH_4 global monitoring.
* Promoting integrated coupled approaches by data assimilation with *in-situ* data and models that will allow taking the best benefits from satellite data.

7.4.3 Modelling

Modelling is considered as an important approach for air quality assessment especially if it is combined with measurements. It is also the only available mean for simulating future climate, pollution events and for understanding their relationships. Some recommendations for increasing confidence in modelling for policy making applications are as follows.

* Reducing uncertainties in coupled systems (air quality and climate) with a better description of dynamics and chemical processes (vertical exchange, cloud chemistry, aerosol properties, urban meteorology);
* Controlling uncertainties describing input parameters in terms of probability distribution functions;
* Improving emission description and quantification, especially biogenic emissions that are particularly sensitive to climate change;
* Developing ensemble systems for focused topics (extreme events for instance) to define the range of possible model responses and assess modelling uncertainties;
* Promoting integrated approaches linking climate, biosphere and atmosphere systems for a better description of fluxes and concentrations.

8. Thanks

We would like particularly to thank the Rapporteurs of the four topic groups, who bore the burden of recording the discussions and recommendations and thus are the prime architects of the workshop's success. We would also like to thank the Plenary Speakers; each provided an excellent overview which set the scene for the subsequent discussions – and the participants for their lively and thoughtful contributions to the discussions. And also the Chairs who highlighted the issues and ensured that there were fair and open discussions.

Out thanks are also due to ACCENT for providing the funds and to the coordinators of the various ACCENT groups, John Burrows, Tony Cox, David, Fowler, Claire Granier, Ivar Isaaksen, Paul Monks and Colin O'Dowd for supporting this ACCENT event.

The staff of the Barnsdale Hall Hotel provided the friendly and helpful front to the excellent facilities which we enjoyed.

Finally we would like to thank Dr. Patricia Borrell for her diligent formatting and correction of the final text of this report.

9 The Plenary Lectures

Impact of Climate Change on Photo-Oxidants, Precursors and Feedback Mechanisms: An Overview of Recent Analyses and Current Issues

Plenary lecture to ACCENT CCAQ: Group 1

Solène Turquety

Université Pierre et Marie Curie-Paris 6, CNRS, Service d'Aéronomie/IPSL, France

Introduction

The increasing emissions of trace gases resulting from human activities have a strong impact on both air quality (locally, on short time scales) and climate (globally, on relatively long time scales). Figure 1 summarizes the main components of the global radiative forcing since 1750 [IPCC, 2007]. In addition to long lived greenhouse gases such as carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O), shorter-lived, reactive species also constitute a major forcing on climate, either as direct climate forcing agents, and/or through their role in tropospheric chemistry. In particular, tropospheric ozone (O_3) is one of the most important greenhouse gases. It is also one of the most harmful pollutants for human health and vegetation growth and is currently regulated by air quality standards worldwide. Air pollution thus plays a major role in global climate change [Jacob *et al.*, 2005]. But climate change also affects air quality, in particular through its impact on photo-oxidant chemistry. The chemical composition of the troposphere is mainly controlled by surface emissions by anthropogenic activities or natural processes, solar radiation, water vapour (H_2O) content, and atmospheric dynamics – factors which are all susceptible to be modified in a changing climate. The strong interaction between atmospheric chemistry and climate is now recognized as a major issue, both for air quality control and climate monitoring. A better understanding of the many feedbacks involved is crucial in order to develop strategies that meet both objectives.

Ozone is a key element of tropospheric chemistry. It is produced by photochemical oxidation of carbon monoxide (CO), CH_4 and non-methane volatile organic compounds (NMVOCs) in the presence of nitrogen oxides (NO_x = NO + NO_2). It is also enhanced by transport from the stratosphere. As the main precursors of the hydroxyl radical (OH), H_2O and O_3 control the oxidizing capacity of the troposphere, and hence its ability to "clean" pollution. Indeed, OH is the main sink for a large variety of species, including CO and VOCs. High ozone pollution episodes mainly occur in the summer, when a greater amount of sunlight increases photochemistry, high temperatures accelerate reactions and stagnant conditions reduce exchanges with clear air. Therefore, both precursors' emissions and meteorological conditions are critical parameters for air quality.

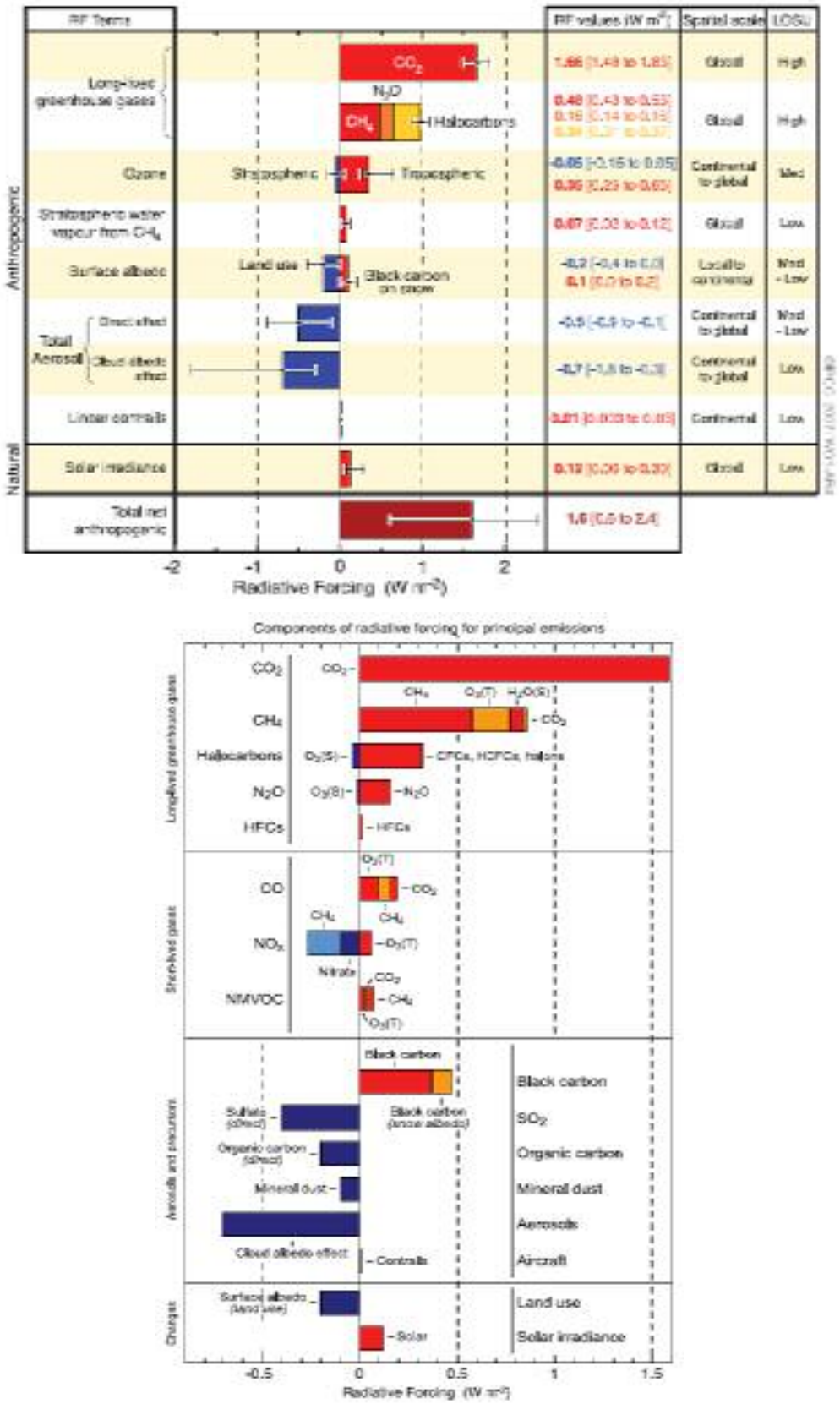


Figure 1. (top) Global mean radiative forcings between 1750 and 2005 for the main agents and mechanisms (bottom) and components for the main emissions [IPCC, 2007].

Analysis of long term observations shows clear evidence for ongoing climate change on several elements of the climate system [IPCC, 2007], some examples are listed below.

Global averaged surface temperatures have increased by 0.74 °C ± 0.18 °C over the past century, with consistent increase in lower and mid-tropospheric temperatures as well as consistent changes in temperature extremes (increase in warm extremes, decrease in cold extremes). The warming rate is faster over continents that over oceans, and greatest at higher northern latitudes during winter and spring.

The frequency and duration of heat waves is increasing (with a record heat-wave over Europe in 2003).

Changes in the large scale atmospheric circulation are observed, with a pole-ward shift of the jet streams and a strengthening of the westerly winds.

Water vapour is increasing throughout the troposphere.

Snow cover has decreased and changes in permafrost and frozen ground have been observed; Vegetation is also adjusting to different climatic conditions.

Precipitation changes depending on the region and season, with clear trends over specific regions: increase over eastern North and South America, northern Europe and northern and central Asia, drying in the Sahel, the Mediterranean, southern Africa and parts of southern Asia. An increase in heavy precipitation events is observed, as well as more intense and longer droughts, particularly in the tropics and subtropics.

Future climate changes are analysed based on climate model simulations using different emission scenarios. An interesting result is that the near-term projections are little affected by different scenario assumptions or different model sensitivities due to committed climate changes, and predict 0.64 to 0.69 °C warming for 2011-2030 relative to 1980-1999.

These climate changes will have a direct impact on surface emissions, reaction rates, atmospheric lifetimes and transport of trace gases, which needs to be better understood and quantified. For example, if increasing temperatures should lead to higher pollution, warmer surface temperatures could also increase turbulence and deepen the planetary boundary layer. Pollution would then be more diluted, which would improve air quality.

In this overview, the results from recent studies of the observed and expected response of atmospheric chemistry to climate change, and of the consequences for air quality, are summarized. The main issues highlighted by these analyses are then discussed.

Impact of climate change on the main ozone precursors

Emission scenarios currently used for climate projections reflect different economic developments, regulation efforts and international cooperation schemes. However, they do not account for possible changes which could result from climate change.

Anthropogenic emissions could be modified due to adjustments to different climate conditions, with, for example, massive use of air-conditioning during heat waves but lower consumption during the winter time, the increasing use of biofuel, *etc*. New emissions may also appear in specific regions. For example, Granier *et al.* [2006] show that emissions of primary pollutants from the opening of shipping routes during the summer in the Arctic could result in strong enhancements of ozone levels over this region.

More importantly, sensitivity of natural emissions to climate change needs to be better accounted for. Emissions of VOCs by vegetation (mainly isoprene and monoterpenes

but also highly reactive chemical species, such as methanol, acetone, aldehydes and organic acids) correspond to ~90 % of the total VOC emissions. They are expected to undergo strong modification, due to changes in land-use (which could also be considered to be an anthropogenic forcing) but also to natural adjustments to new climatic conditions: increasing temperature, different precipitation pattern in particular. For example, Lathière *et al.* [2005] use a global dynamical vegetation model to evaluate biogenic VOC emissions and their evolution with climate change. Figure 2 shows the predicted evolution in vegetation cover (leaf area index LAI) and derived emissions of isoprene and monoterpenes. Emissions of biogenic VOCs globally increase due to larger LAI and higher temperatures, except over the Amazon Basin, where a recession of tropical forest is predicted.

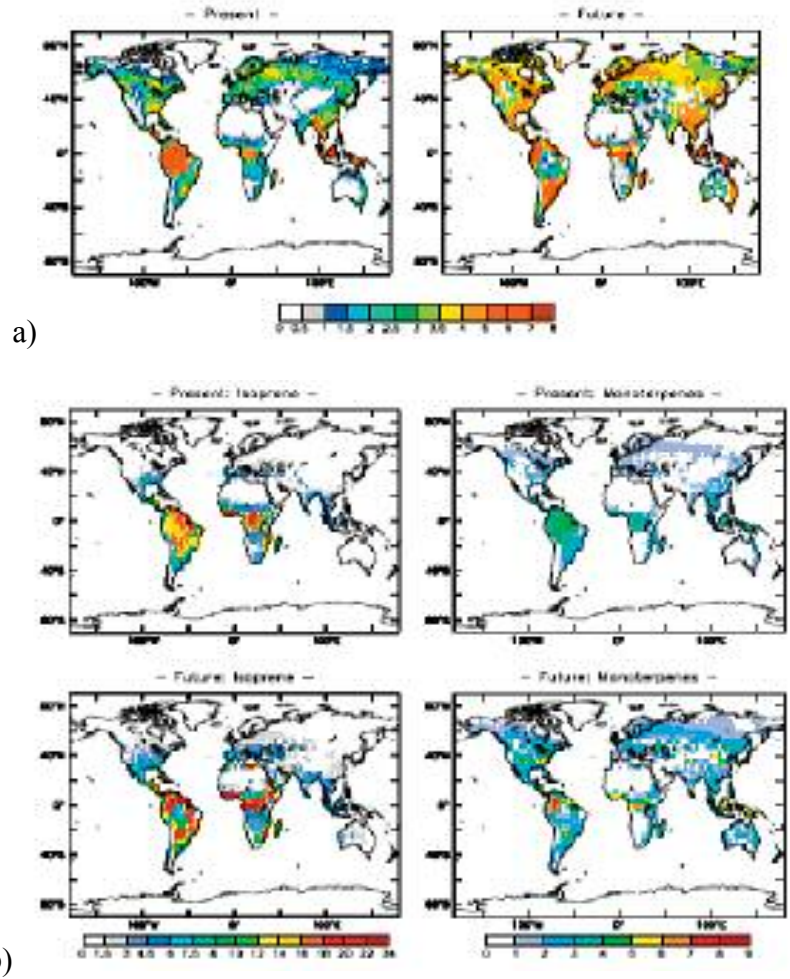


Figure 2. a) Yearly mean global changes in leaf area index (m^2/m^2) between 1990 and 2100; b) Corresponding changes in isoprene and monoterpenes (gC/m^2/month) [Lathière *et al.*, 2005].

Further study of the impact of land-use changes shows that tropical deforestation induces a global decrease of 29 % of the isoprene emissions and an increase of 22 % of the methanol emissions (from croplands) [Lathière *et al.*, 2006]. On the contrary, afforestation in Europe leads to an increase of 54 % of VOC emissions over Europe. However, the adjustment of vegetation as a result of new climatic conditions (type of trees, *etc*.) remains very uncertain. Moreover, such mutation could be mitigated (to some degree) by specific strategies to maintain regional biodiversity, which can not be accounted for in models.

Changes in natural NO_x emissions are also expected. Lightning is a significant source of NO_x in the free troposphere, directly associated with convection, and with strong implication for tropospheric chemistry [Hudman *et al.*, 2007]. More intense convective activity could result in significantly enhanced lightning NO_x emissions [Hauglustaine *et al.*, 2005, Brasseur *et al.*, 2006]. However, the parameterization of convection and the amount of NO_x emitted remains highly uncertain.

Soils are also an important natural source of NO_x during the wet season, in particular in the tropics. Large pulses of biogenic NO emissions are observed following heavy rainfalls on dry soil, which activate water-stressed nitrifying bacteria (the consumption of accumulated nitrogen leading to NO emissions). NO emissions remain relatively high during the whole wet season. Soil NO_x emissions are still poorly understood and quantified, and greatly underestimated in current inventories [Jaeglé *et al.*, 2004]. These emissions are affected by land-use (fertilizer use in particular), but also by climate. According to the IPCC report, precipitation events will be more frequent, and the dry periods between rainfalls will be more important, which could favour biogenic emissions from soils. Estimation from dynamical vegetation model suggests possible increase of about 20 % by 2100 [Hauglustaine *et al*., 2005]. This could be a significant factor over remote regions and in the tropics.

For CH_4, the dominant natural source is wetlands, which represent about a third of the total emissions. Shindell *et al.* [2004] evaluate the evolution of wetland CH_4 emissions using a simplified emission model within a GCM with a doubled CO_2 scenario. They find that warmer temperatures and enhanced precipitations lead to the expansion of wetlands (areas and depth), inducing an average increase of 78 %, which represents 20 % of the current total CH_4 emissions. The wetland emissions more than double during the summer, in particular over the northern hemisphere high latitudes due to accelerating rates of permafrost thaw. The melting of the permafrost could also release large quantities of carbon, stored in the peatlands, but large vegetation productivity in the flooded areas could also act as a larger carbon sink [Turetsky *et al.*, 2007].

Biomass burning constitutes a large source of emissions for a series of trace gases and aerosols, which is responsible for a large fraction of interannual variations of tropospheric concentrations [Wotawa *et al.*, 2001; Szopa *et al.*, 2007]. Warmer and drier conditions will significantly increase the fire risk in many regions. For example, intense burning in southern Europe and the Mediterranean regularly occurring during the summer significantly degrade local air quality over large regions. Wildfires in boreal forest are also important for air quality, locally but also continental and even hemispheric scales. Large emissions from wildfires in Alaska and Canada during the summer of 2004 [Turquety *et al.*, 2007] had consequences for air quality as far as the southern United-States [Morris *et al.*, 2006] and Europe [Cook *et al.*, 2007; Real *et al.*, 2007]. These large boreal fires are expected to increase as a result of climate change due to earlier snow melt, warmer and dryer conditions [Gillett *et al.*, 2004]. As already mentioned, large quantities of carbon are stored in the boreal soils. Fires in peatlands release large quantities of pollutants which are not currently accounted for in inventories [Turquety *et al.*, 2007], and this contribution could significantly increase in the future. However, the impact and evolution of fire emissions is extremely difficult to predict due to the variable character of these events, to the large uncertainties on surface emissions inventories, but also on the evolution of vegetation cover.

These examples show that a significant increase of direct emissions of primary pollutants and ozone precursors is expected as a result of climate change. This climate impact on emissions is currently not well quantified in most model simulations. However, the net effect of climate on atmospheric concentrations of these pollutants is

more difficult to assess. Indeed, these concentrations depend critically on chemistry, and on OH levels in particular since OH is the main sink for CO and VOCs. A warmer climate implies larger HO_2, leading to larger OH. Increasing O_3 and NO_x also result in increasing OH. On the contrary, increasing CO, CH_4 and VOCs results in decreasing OH concentrations. It is therefore difficult to predict variations in OH concentrations. Methyl chloroform observations indicate growing OH levels until the late 1980s followed by clear decrease in the 1990s [Prinn *et al.*, 2001]. Trends in CH_4 show consistent increase in the 1990s, and levelling off after 1998, which can be attributed to variations in OH, possibly due to an increase in lightning NO_x, but also in surface emissions [Fiore *et al.*, 2006].

Projections for the future indicate decreasing OH associated with increasing emissions (with a magnitude depending on the scenarios) but an increase associated with increasing H_2O [Stevenson *et al.*, 2006], so that the global change is low [Hauglustaine *et al.*, 2005]. For CO, the multi-model ensemble analysis presented by Shindell *et al.* [2006] shows that, while increasing emissions lead to larger CO, climate change only (not including subsequent emissions changes) results in a global decrease of CO in most model projections.

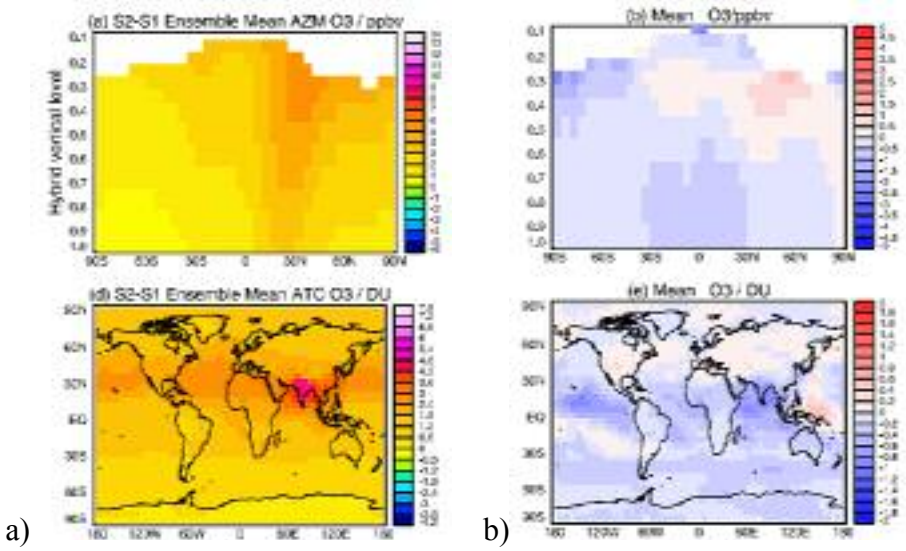
Impact of climate change on global ozone

Ozone trends are difficult to analyse due to sparse *in situ* observations and the lack of long term records. Oltmans *et al.* [2006] analysed long-term variations using long record of *in situ* observations. The derived trends vary strongly depending on the location and altitude of the measurements. In the southern hemisphere, time series show increases up to the mid-troposphere. In the northern hemisphere high latitudes, small positive trend in recent decade seems mainly related to changes in the lowermost stratosphere. In the mid-latitudes, continental tropospheric ozone increased significantly in the 1970s and 1980s, but remained stabled or decreased in the more recent decades, while a significant increase is still observed over the North Atlantic. In the tropics, significant increase is attributed to a shift in the transport pattern during this season with more frequent flow from higher latitudes in the latest decade.

Several analyses based on coupled chemistry-climate models have been conducted in order to assess the variations of ozone since pre-industrial levels, as well as the expected trends in the future. These global models allow the analysis of specific signatures associated with the different changes, in particular surface emissions and climate modifications. A multi-model analysis of tropospheric ozone radiative forcing since preindustrial times was led within the ACCENT network [Gauss *et al.*, 2006]. All models show significant increase of tropospheric ozone and decrease of stratospheric ozone as a result of changes in surface emissions and chemistry. Accounting for the response of climate change implies further increase in the troposphere and a reduction of the stratospheric decrease. Taking into account both the troposphere and the stratosphere results in decreasing total ozone amounts, but the resulting total ozone radiative forcing is still increasing.

Recent studies analysed the respective impact of future emissions scenarios and of future climate change on tropospheric chemistry [Hauglustaine *et al.*, 2005; Brasseur *et al.,* 2006; Stevenson *et al.*, 2006]. These experiments predict global increase of tropospheric ozone throughout the troposphere (example shown in Figure 3 for the multi-model ensemble analysis of Stevenson *et al.* based on the current legislation scenario, resulting in 6 % total increase), except for most optimistic emissions scenarios (5% decrease for the maximum reduction scenario). Most models show significant increase of ozone levels associated with increasing biogenic emissions. For example,

Hauglustaine *et al.* [2005] show up to 50% increase in surface ozone by the end of the century in northern America, western Europe and northern China during the summer. However, large increase in isoprene emissions could also result in decreasing ozone in some regions, such as the southeastern United-States [Wu *et al.*, 2007a] due to the sequestration of NO_x as isoprene nitrates and isoprene ozonolysis.



a) b)

Figure 3. Multi-model ensemble average ozone changes between 2000 and 2030 due to: a) changes in emissions only (based on current legislation scenario, CLE) and b) climate change only (difference between simulations with CLE and year 2030 climate and simulations with CLE and year 2000 climate) [Stevenson *et al.*, 2006].

Climate change partly offsets the increase associated with larger emissions, with expected global reduction in ozone levels due to larger OH levels (wetter climate). The largest feedback is predicted in the tropics, particularly over the ocean. However, some models predict increased ozone levels over the continents resulting from enhanced ozone production due to larger PAN decomposition with increasing temperature [Hauglustaine *et al.*, 2005]. On the other hand, shorter PAN lifetime reduces the impact of long range transport on ozone production. Upper tropospheric ozone is expected to increase in response to climate change due to larger stratospheric influx and increased lightning NO_x emissions. This could result in increasing total climate forcing since the impact of upper tropospheric ozone on climate is larger. Impact of increased OH levels also influences CH_4 lifetime, and a reduction of this parameter could lower radiative forcing.

Expected impact on local air quality

Regulation policies for air quality improvement have led to significant emission reduction over the main developed countries. Consistently, surface observations over these regions seem to indicate negative trends in surface ozone maxima in the summer [Oltmans *et al.*, 2006; Vautard *et al.,* 2006]. However, measurements in Canada and the United States show clear increase in surface ozone in the past decades [Vingarzan, 2004]. Trends in ozone observations are difficult to analyse due to competing influences. Moreover, as previously discussed, significant changes of the tropospheric chemical composition are expected as results of climate change on a global scale. From an air quality perspective, surface pollution is also sensitive to climate change and will be modified in the future.

Several recent studies investigated the sensitivity of air quality (surface ozone average and daily maxima in particular) to climate change using chemistry-climate modelling. Szopa *et al.* [2006] analysed the impact of global anthropogenic emission changes on European air quality using a downscaling from a global to a regional chemistry-transport model. Current legislation emission scenarios indicate a global increase of anthropogenic emissions, but a decrease of European contribution. Previous analysis showed the ability of the regional model to reproduce recent trends in surface ozone [Vautard *et al.*, 2007]. Szopa *et al.* find that future surface ozone increases in northern Europe and decreases in parts of southern and central Europe, showing that emission control in Europe is competing with the influence from increasing background levels. However, they find that ozone maxima are significantly reduced (Figure 4). In addition to surface emissions changes, the effect of climate change needs to be considered. As detailed in the previous section, enhanced water vapour results in a decrease in ozone levels, which could partly compensate the increased background. Increasing biogenic emissions could also be critical for air quality. Larger temperatures also induce faster chemical reactions, and shorter lifetimes for some key species as PAN, with direct influence on local ozone production.

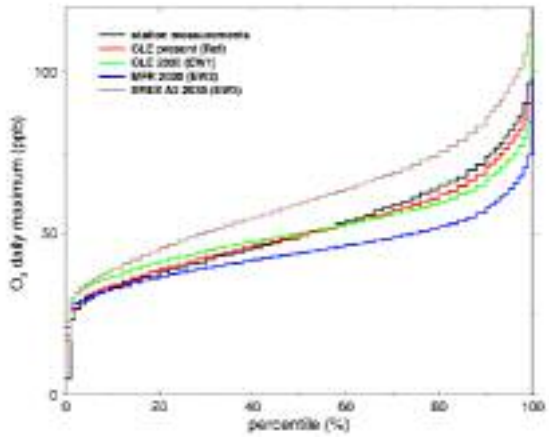


Figure 4. Daily O_3 maximum percentiles distribution over 244 European ground based stations using 2001 measurements (black) and for CHIMERE regional model simulation for present-day run (red); and 2030 with different emissions scenarios [Szopa *et al.*, 2007].

Modification of meteorological conditions is also an important factor for the development of pollution episodes. Mickley *et al.* [2004] show that the duration of pollution episodes could increase from ~2 to ~3 to 4 days in the US due to lower frequency of mid-latitude cyclones, and resulting decrease of the ventilation by cold fronts, which is already apparent in long-term observations. They also find an increase in the depth of the boundary layer, which tends to improve air quality but remains low compared to the increased stagnation. Longer episodes are also expected over Europe [Hauglustaine *et al*., 2005], whereas enhanced monsoon over India and Southeast Asia would, on contrary, increase boundary layer venting and improve air quality.

Such complex interactions are difficult to predict, but are crucial for the development of efficient strategies which will benefit to both air quality and climate. Sensitivity analysis of the influence of different emission control strategies show that, although surface ozone pollution depends mainly on NO_x levels, reducing CH_4 emissions in the best compromise [West *et al.*, 2007]. Indeed, short terms improvements from NO_x, CO or NMVOC limitation are concentrated near source regions. Reduction of NO_x and CH_4 lead to the largest decrease of surface ozone levels. NMVOC reduction efficiency is limited mainly by large biogenic sources. In some regions, NO_x reduction increases

surface ozone due to lower ozone destruction. It also causes a long-term increase in CH_4, and thereby enhances radiative forcing as well as surface ozone. The interaction between chemistry, aerosols and climate also needs to be better understood and accounted for. Brasseur and Roeckner [2005] show, for instance, that global temperature and precipitation change would be greatly enhanced by strong reduction of anthropogenic sulfate aerosols.

Current issues: how accurately can we predict the impact of climate change on tropospheric chemistry?

Analyses of the expected impact of climate change are mainly undertaken based on complex coupled chemistry and climate models, which allow detailed analysis of the different processes involved and projections for expected future conditions. Multi-model ensemble analyses are undertaken in order to provide robust conclusions as well as an assessment of uncertainties associated with the predictions.

Comparisons between present-day model predictions and observations highlight the current uncertainties, even for relatively well known and extensively observed species like CO [Shindell *et al.*, 2006] and ozone [Gauss *et al*., 2006; Stevenson *et al.*, 2006]. Current results show systematic underestimate of CO in the Northern Hemisphere compared to observations, which is mainly attributed to strongly under-estimated Asian emissions. Underestimate of production from VOC oxidation could also be partly responsible.

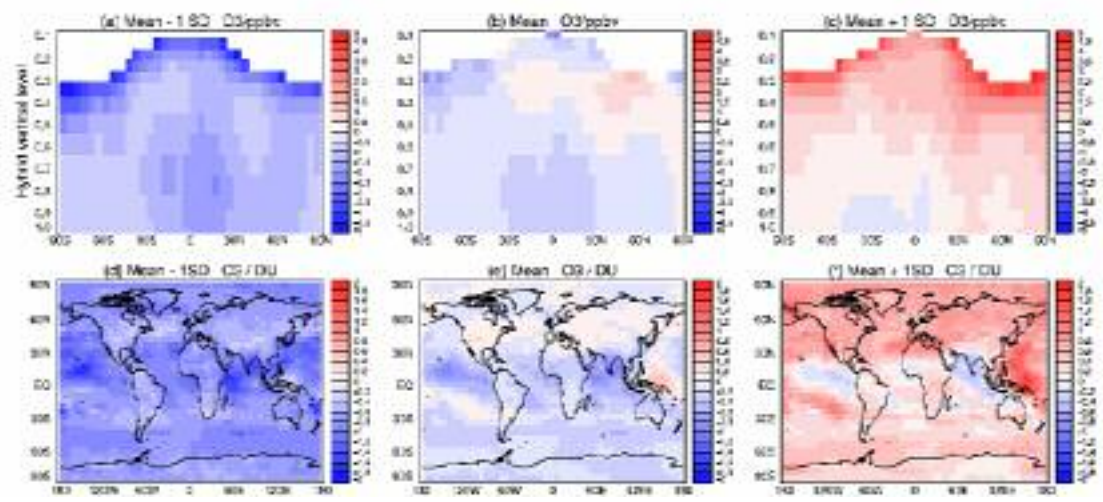


Figure 5. Multi-model ensemble mean ozone changes due to climate change (same as Figure 3). The ensemble plus and minus 1 standard deviation are also shown [Stevenson *et al.*, 2006].

These multi-model analyses also highlight large discrepancies between models (using the same surface emissions), which can change the magnitude of the calculated trends, and even their sign. As an illustration, Figure 5 shows the mean and standard deviation in the global ozone changes from the multi-model analysis by Stevenson *et al.* [2006] shown in Figure 3. Simulated changes have typical uncertainties of 20-35 %. The base simulations for 2000 were compared to ozone sonde measurements in order to evaluate model performance. The average comparison shows good agreement, but the deviation between different models is large. The large standard deviation in the model response can be attributed to differences in the simulation of several key processes: parameterization of deep convection, and the associated lightning NO_x emissions, inclusion of NMVOCs, in particular biogenic isoprene emissions and related chemistry, stratosphere-troposphere exchanges, predictions of biomass burning emissions, and H_2O

concentrations. This is consistent with detailed analysis conducted by Wu *et al.* [2007b] using simulations from different CTMs, and the same CTM with different meteorological fields.

While numerical simulations of chemistry and climate are necessary to improve our understanding of the key processes and feedback mechanisms, and help us envision the impact of different strategies, model results should systematically be confronted to atmospheric measurements for robust analyses. Past trends can provide an insight onto ongoing changes, and in depth analysis of observations during extreme events, such as the record-breaking heat wave in Europe in 2003, allow better understanding of processes which are susceptible to prevail in the future.

Recent satellite missions dedicated to the observation of the troposphere provide extremely useful new means of monitoring the evolution of chemical composition, with unprecedented global observations for several key species. Various satellite data analyses have helped evaluate current emission inventories. In particular, they show that large emission regions may be greatly underestimated for several species, including key species such as CH_4, CO, NO_x, isoprene and methanol [Pétron *et al*., 2004; Jaeglé *et al.*, 2005; Palmer *et al.*, 2006; Bergamaschi *et al.*, 2007; Dufour *et al.*, 2007]. In addition to providing interesting constraints on surface emissions and atmospheric concentrations, records are now long enough to analyse recent trends [Richter *et al.*, 2005]. METOP-A, launched in 2006, is the first of a series of three satellites which should provide at least 15 years of consistent measurements. It carries two complementary instruments, IASI measuring in the thermal infrared spectral region and GOME-2 in the UV-visible, which will allow simultaneous observations of ozone, CO, NO_2, formaldehyde, CH_4 and CO_2 and possibly more reactive species such as nitric acid [Turquety *et al.*, 2004; http://www.iup.uni-bremen.de/doas/gome2_first_results.htm], as well as meteorological parameters (H_2O, temperature, clouds, *etc*.) These measurements will offer an unprecedented picture of tropospheric chemistry and its evolution.

References

Bergamaschi, P., *et al*., Satellite chartography of atmospheric methane from SCIAMACHY on board ENVISAT: 2. Evaluation based on inverse model simulations, *J. Geophys. Res.*, **112**, D02304, doi:10.1029/2006JD007268, 2007.

Brasseur, G. P., and E. Roeckner, Impact of improved air quality on the future evolution of climate, *Geophys. Res. Lett.*, **32**, L23704, doi:10.1029/2005GL023902, 2005.

Brasseur, G. P., M. Schultz, C. Granier, M. Saunois, T. Diehl, M. Botzet, E. Roeckner, and S. Walters, Impact of Climate Change on the Future Chemical Composition of the Global Troposphere, *Journal of Climate*, **19**, 16, 3932–3951, doi: 10.1175/JCLI3832.1, 2006.

Cooper, O. R., *et al.,* Large upper tropospheric ozone enhancements above mid-latitude North America during summer: In situ evidence from the IONS and MOZAIC ozone monitoring network, *J. Geophys. Res.*, **111**, D24S05, doi:10.1029/2006JD007306, 2006.

Cook, P. A., *et al*., Forest fire plumes over the North Atlantic: p-TOMCAT model simulations with aircraft and satellite measurements from the ITOP/ICARTT campaign, *J. Geophys. Res.*, **112**, D10S43, doi:10.1029/2006JD007563, 2007.

Fiore, A. M., L. W. Horowitz, E. J. Dlugokencky, and J. J. West, Impact of meteorology and emissions on methane trends, 1990–2004, *Geophys. Res. Lett*., **33**, L12809, doi:10.1029/2006GL02619, 2006.

Gillett, N. P., A. J. Weaver, F. W. Zwiers, and M. D. Flannigan, Detecting the effect of climate change on Canadian forest fires, *Geophys. Res. Lett*., **31**, L18211, doi:10.1029/2004GL020876, 2004.

Granier, C., U. Niemeier, J. H. Jungclaus, L. Emmons, P. G. Hess, J.-F. Lamarque, S. Walters, and G. P. Brasseur, Ozone pollution from future ship traffic in the Arctic northern passages, *Geophys. Res. Lett.*, **33**, L13807, doi:10.1029/2006GL026180, 2006.

Hauglustaine, D. A., J. Lathière, S. Szopa, and G. A. Folberth, Future tropospheric ozone simulated with a climate-chemistry-biosphere model, Geophys. Res. Lett., **32**, L24807, doi:10.1029/2005GL024031, 2005.

Hudman, R.C., *et al*., Surface and lightning sources of nitrogen oxides in the United States: magnitudes, chemical evolution, and outflow, *J. Geophys. Res.,* **112**, D12S05, doi:10.1029/2006JD007912, 2007.

Intergovernmental Panel on Climate Change (IPCC), Climate Change 2007: The Physical Science Basis, edited by S. Solomon, D. Qin, and M. Manning, Geneva, 2007.

Jacob, D.J., and A.B. Gilliland, Modelling the impact of air pollution on global climate change, *Environmental Manager*, pp. 24-27, 2005.

Lathière, J., D. A. Hauglustaine, N. De Noblet-Ducoudré, G. Krinner, and G. A. Folberth, Past and future changes in biogenic volatile organic compound emissions simulated with a global dynamic vegetation model, *Geophys. Res. Lett*., **32**, L20818, doi:10.1029/2005GL024164, 2005.

Lathière, J., D. A. Hauglustaine, A. D. Friend, N. De Noblet-Ducoudré, N. Viovy, and G. A. Folberth, Impact of climate variability and land use changes on global biogenic volatile organic compound emissions, *Atmos. Chem. Phys.*, **6**, 2129-2146, 2006.

Mickley, L. J., D. J. Jacob, B. D. Field, and D. Rind , Effects of future climate change on regional air pollution episodes in the United States, *Geophys. Res. Lett*., **31**, L24103, doi:10.1029/2004GL021216, 2004.

Morris, G. A*., et al*., Alaskan and Canadian forest fires exacerbate ozone pollution over Houston, Texas, on 19 and 20 July 2004, *J. Geophys. Res*., **111**, D24S03, doi:10.1029/2006JD007090, 2006.

Palmer, P.I., *et al*., Quantifying the seasonal and interannual variability of North American isoprene emissions using satellite observations of the formaldehyde column, *J. Geophys. Res.*, **111** (D12), D12315, 41 doi:10.1029/2005JD006689, 2006.

Pétron, G., C. Granier, B. Khattatov, V. Yudin, J. Lamarque, L. Emmons, J. Gille, and D. P. Edwards, Monthly CO surface sources inventory based on the 2000–2001 MOPITT satellite data, *Geophys. Res. Lett*., **31**, L21107, doi:10.1029/2004GL020560, 2004.

Prinn, R. G., J. Huang, R. F. Weiss, D. M. Cunnold, P. J. Fraser, P. G. Simmonds, A. McCulloch, C. Harth, P. Salameh, S. O'Doherty, R. H. J. Wang, L. Porter, and B. R. Miller, Evidence for Substantial Variations of Atmospheric Hydroxyl Radicals in the Past Two Decades, *Science*, 1882-1888, doi: 10.1126/science.1058673, 2001.

Richter, A., J. P. Burrows, H. Nüß, C. Granier and U. Niemeier, Increase in tropospheric nitrogen dioxide over China observed from space, *Nature*, **437**, 1, doi:10.1038/nature04092, 2005.

Real E., *et al.*, Processes influencing ozone levels in Alaskan forest fire plumes during long-range transport over the North Atlantic*, J. Geophys. Res.*, **112**, D10S41, doi:10.1029/2006JD007566, 2007.

Shindell, D. T., B. P. Walter, and G. Faluvegi, Impacts of climate change on methane emissions from wetlands, *Geophys. Res. Lett.*, **31**, L21202, doi:10.1029/2004GL021009, 2004.

Shindell, D. T., *et al*., Multimodel simulations of carbon monoxide: Comparison with observations and projected near-future changes, *J. Geophys. Res.*, **111**, D19306, doi:10.1029/2006JD007100, 2006.

Stevenson, D. S., *et al.*, 2006, Multimodel ensemble simulations of present-day and near-future tropospheric ozone, J. Geophys. Res., **111**, D08301, doi:10.1029/2005JD006338, 2006.

Szopa, S., D. A. Hauglustaine, R. Vautard, and L. Menut, Future global tropospheric ozone changes and impact on European air quality, *Geophys. Res. Lett.,* **33**, L14805, doi:10.1029/2006GL02586, 2006.

Szopa, S., D. A. Hauglustaine, and P. Ciais, 2007, Relative contributions of biomass burning emissions and atmospheric transport to carbon monoxide interannual variability, *Geophys. Res. Lett*., **34**, L18810, doi:10.1029/2007GL030231.

Turquety, S., J. Hadji-Lazaro, C. Clerbaux, D. A. Hauglustaine, S. A. Clough, V. Cassé, P. Shlüssel, and G. Mégie, Trace gas retrieval algorithm for the Infrared Atmospheric Sounding Interferometer, *J. Geophys. Res*., **109**, D21301, 10.1029/2004JD00482, 2004.

Turquety, S., J.A. Logan, D.J. Jacob, R.C. Hudman, F.Y. Leung, C.L. Heald, R. M. Yantosca, S. Wu, L. K. Emmons, D.P. Edwards, and G.W. Sachse, 2007, Inventory of boreal fire emissions for North America in 2004: the importance of peat burning and pyro-convective injection, *J. Geophys. Res*., **112**; D12S03; doi:10.1029/2006JD007281, 2007.

Turetsky, M.R., R.K. Wieder, D.H. Vitt, R. Evans, and K. D. Scott, The disappearance of relict permafrost in boreal regions: effects on peatland carbon storage and fluxes, *Global Change Biology* **13**: 1-13, 2007.

Vautard, R., S. Szopa, M. Beekmann, L. Menut, D. A. Hauglustaine, L. Rouil, and M. Roemer, Are decadal anthropogenic emission reductions in Europe consistent with surface ozone observations?, *Geophys. Res. Lett*., **33**, L13810, doi:10.1029/2006GL026080, 2006.

Vingarzan, R., A review of surface ozone background levels and trends, *Atmos. Environ*., **38**, 3431–3442, 2004.

Wespes C., D. Hurtmans, H. Herbin, B. Barret, S. Turquety, J. Hadji-Lazaro, C. Clerbaux, P.-F. Coheur, First global distributions of nitric acid in the troposphere and the stratosphere derived from infrared satellite measurements, *J. Geophys. Res*., **112**, D13311, doi:10.1029/2006JD008202, 2007.

West, J. J., A. M. Fiore, V. Naik, L. W. Horowitz, M. D. Schwarzkopf, and D. L. Mauzerall, Ozone air quality and radiative forcing consequences of changes in ozone precursor emissions*, Geophys. Res. Lett.,* **34**, L06806, doi:10.1029/2006GL029173, 2007.

Wotawa, G., P. C. Novelli, M. Trainer and C. Granier, Inter-annual variability of summertime CO concentrations in the Northern Hemisphere explained by boreal forest fires in North America and Russia, *Geophys. Res. Lett.*, **28**, 24, 4575-4578, 2001.

Wu, S., L.J. Mickley, E.M. Leibensperger, D.J. Jacob, D. Rind and D.G. Streets, Effects of 2000-2050 global change on ozone air quality in the United States, *J. Geophys. Res*., in press, 2007a.

Wu, S., L. J. Mickley, D. J. Jacob, J. A. Logan, R. M. Yantosca, and D. Rind, Why are there large differences between models in global budgets of tropospheric ozone?, *J. Geophys. Res*., **112**, D05302, doi:10.1029/2006JD007801, 2007b.

Surface−Atmosphere Interactions

Plenary lecture to ACCENT CCAQ: Group 2

William Collins

Met Office Hadley Centre, UK

Introduction

Air Quality and climate are intimately connected and are both part of the coupled earth system. Air quality is determined by four processes: the emission of pollutants, their transport, their transformation and their removal. In this paper we will focus principally on ozone which is an air quality pollutant affecting human health and plant growth [Ashmore 2005]. It is also a climate warming gas. Ozone is principally a secondary pollutant in that it is formed in the atmosphere by photochemical reactions in the atmosphere involving oxides of nitrogen (NO_X) and volatile organic compounds (VOCs). It is destroyed by reactions involving water vapour, and is removed by contact with the earth's surface.

Anthropogenic emissions can vary with temperature, either directly due to changes in volatilization, or indirectly through changes in behaviour such as energy usage. Natural emissions can be very sensitive to meteorology, depending on sunlight, temperature, precipitation and CO_2 levels. Air quality is very sensitive to changes in transport. Pollution events are most associated with stable high pressure anticyclonic systems. These trap pollutants below an inversion layer where they accumulate. High pressure systems affect the transformation of pollutants too. They generally have little cloud cover, providing plenty of sunlight and higher temperatures for the photochemical reactions. Removal by precipitation is obviously dependent on meteorology. Removal at the earth's surface can depend on the physical meteorology (wind speed and turbulence) but also on the overlying vegetation.

We have not yet reached levels of climate change large enough to determine directly its effect on air pollution. One indirect way of doing this is to use heatwaves as analogies for climate change. There was a major heatwave in Europe during the first two weeks of August 2003 when temperatures in the UK peaked at a record 38.5 °C. Stedman [2004] attributed between 423 and 763 excess deaths due to high air pollution in England and Wales during this period. Climate predictions by Stott *et al.* [2004] show that by 2040 half the years will see warmer summers in Europe than 2003 (Figure 1).

It is not clear how far the heatwave analogues can be taken. Not only were the temperatures high over Europe in August 2003, the intense high pressure system lead to an increase in the accumulation of pollutants. Thus a global increase in temperature by 2040 might not lead to similar levels of pollution if the temperature increase was not accompanied by an increase in the frequency or intensity of high pressure systems. Another way of predicting the effect of future climate on atmospheric chemistry and air quality is by using global chemistry models. Johnson *et al*. [2001] used such a model to show that increased humidity in a warmer climate would lead to increased tropospheric ozone destruction and hence a lower ozone burden.

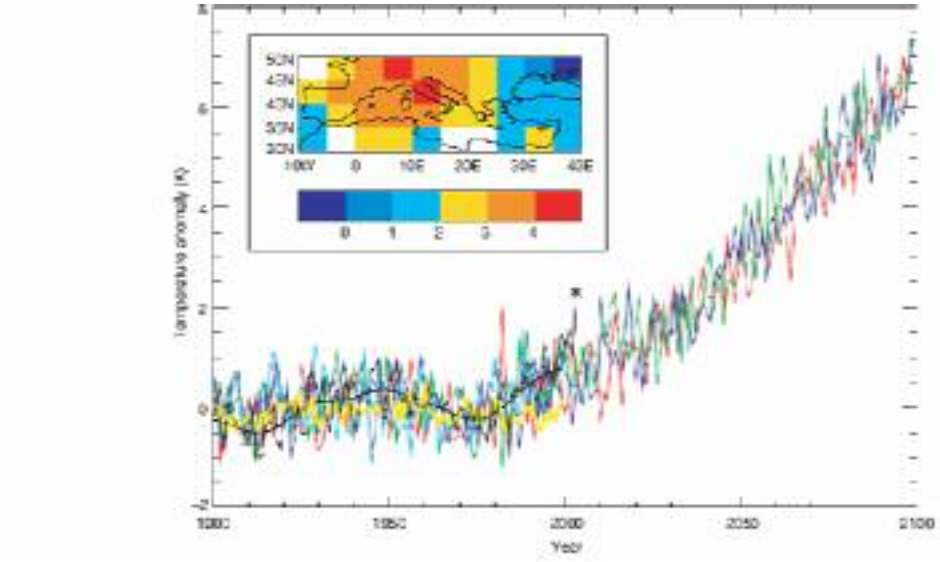


Figure 1. Observed and simulated European June-August temperature anomalies relative to the 1961 – 1990 mean [Stott *et al*., 2004]. The asterisk marks the 2003 anomaly.

Figure 2 shows two simulations of the ozone burden changing with anthropogenic emissions of NO_X and VOCs over the 21st century. The black dots are for a constant climate and show a steep increase over the course of the century as the emissions increase. The red dots show that when future climate change is considered, the increase is far less steep.

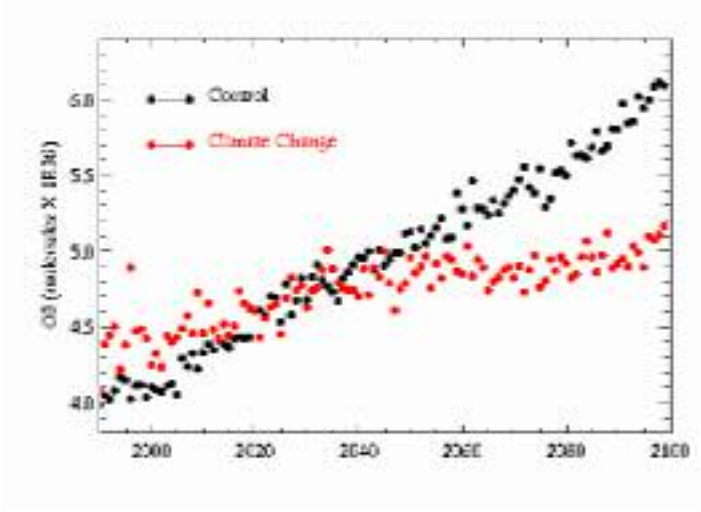


Figure 2. The predicted evolution of the tropospheric ozone burden with a constant (control) and changing climate [Johnson *et al.* 2001].

With a warmer climate, the exchange between the stratosphere and troposphere is expected to increase [Butchart and Scaife 2001]. Surface warming due to increased CO_2 leads to a cooler lower stratosphere, and less destruction of lower stratospheric ozone (except for at the poles). Chemistry models have found that this increased circulation combined with the increase in lower stratospheric ozone leads to significantly more stratospheric ozone being transported into the troposphere [Collins *et al.* 2003, Zeng and Pyle 2003, Sudo *et al*. 2003]. Figure 3 shows simulated surface ozone concentrations and the stratospheric contribution at Mace Head in Ireland for current and future climate.

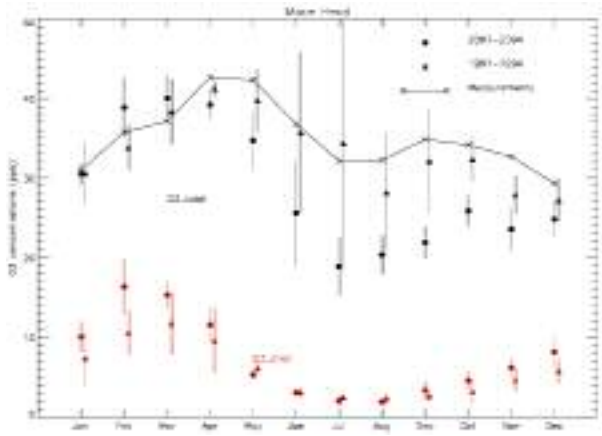


Figure 3. The simulated influence of climate change on surface ozone and the stratospheric contribution at Mace Head, Ireland [Collins *et al*. 2003].

The increased humidity and increased stratosphere-troposphere exchange (STE) act in opposite directions. The first process decreases ozone, the second increases it. Stevenson et al. [2006] looked at the effect of climate change on ozone predicted by 10 global tropospheric chemistry models. The results are shown in Figure 4. On average the models predicted almost no change in the tropospheric ozone budget as the humidity and STE effects approximately cancel. However, there was a large spread in the model results, with some models predicting significant decreases and some significant increases. Few of these models incorporated the effects of climate on biogenic emissions of ozone precursors, and none of them considered the effects of climate on the removal of ozone by vegetation. The coupling between chemistry and ecosystems may be a significant feedback mechanism between climate change and atmospheric chemistry and air quality.

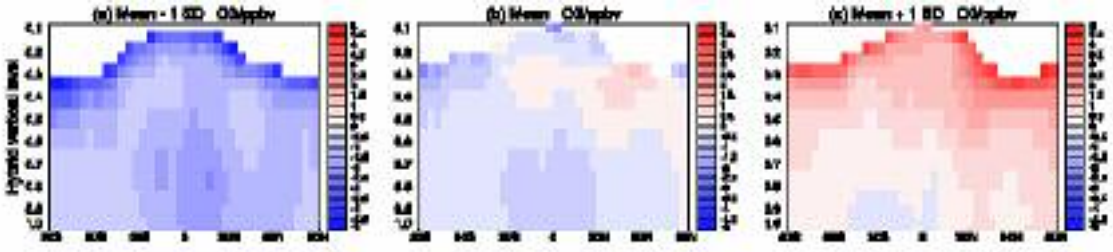


Figure 4. The simulated influence of climate change on the zonal cross-section of tropospheric ozone. (b) shows the mean of 10 models, (a) and (c) show the mean -/+ 1 standard deviation within the model ensemble. Figure from Stevenson *et al.* [2006].

Coupling between atmosphere and the surface via ecosystems.

As described above, the surface is the major source of ozone precursors, and is a significant sink for ozone. The most important climate influences on the surface sources and sinks are where these processes involve ecosystems, since ecosystems are highly sensitive to climate.

The importance of the link between chemistry and ecosystems has been long established. The emissions of isoprene from vegetation [Guenther *et al*. 1995], NO_X from soils [Yienger and Levy 1995] and methane from wetlands [Aselmann and Crutzen 1989], are widely used in tropospheric chemistry models. These emissions can be dependent on meteorological variables such as temperature, insolation and precipitation, but also on ecosystem variables such as soil and vegetation amounts and types. In a future climate, these meteorological and ecosystem variables are likely to have changed considerably [Cox *et al.* 2000] leading to significantly different natural emissions than measured today [Sanderson *et al.* 2003a, Gedney *et a*l. 2004]. Thus changes in natural emissions need to be taken in to account when predicting future atmospheric composition and air quality. Figure 5 shows the variation in the concentrations of isoprene and its degradation products measured at a site in the east of England in a period covering the start of the August 2003 heatwave. Much larger isoprene concentrations were measured during the heatwave than before it. Highly elevated ozone concentrations were observed at the same time. Lee *et al.* [2006] conclude that although most of the elevated ozone was advected to the site from continental Europe, *in-situ* production of ozone from the increased isoprene could have contributed to the pollution episode. It is not known whether this isoprene response would be the same under constantly elevated temperatures in a warmer climate, or whether vegetation would acclimatise.

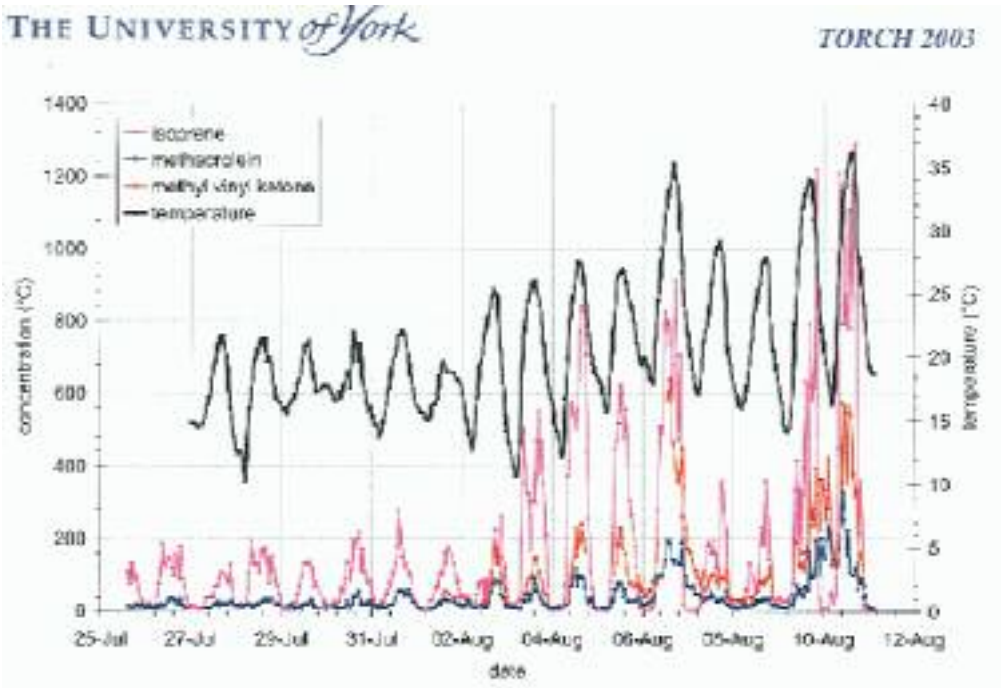


Figure 5. The variation of temperature and isoprene and its degradation products at a site in eastern England in 2003 [Lee *et al.* 2006].

Wetlands contribute around a third of the emissions of methane into the atmosphere. The emissions increase with temperature. In a modelling study, Gedney *et al*. [2004] predicted that these emissions could increase by about 200 Tg/yr for a 4.2 K temperature rise. These emissions are shown in Figure 6. This study focussed on methane as a climate forcing gas, but methane also contributes significantly to surface ozone pollution [West and Fiore 2005].

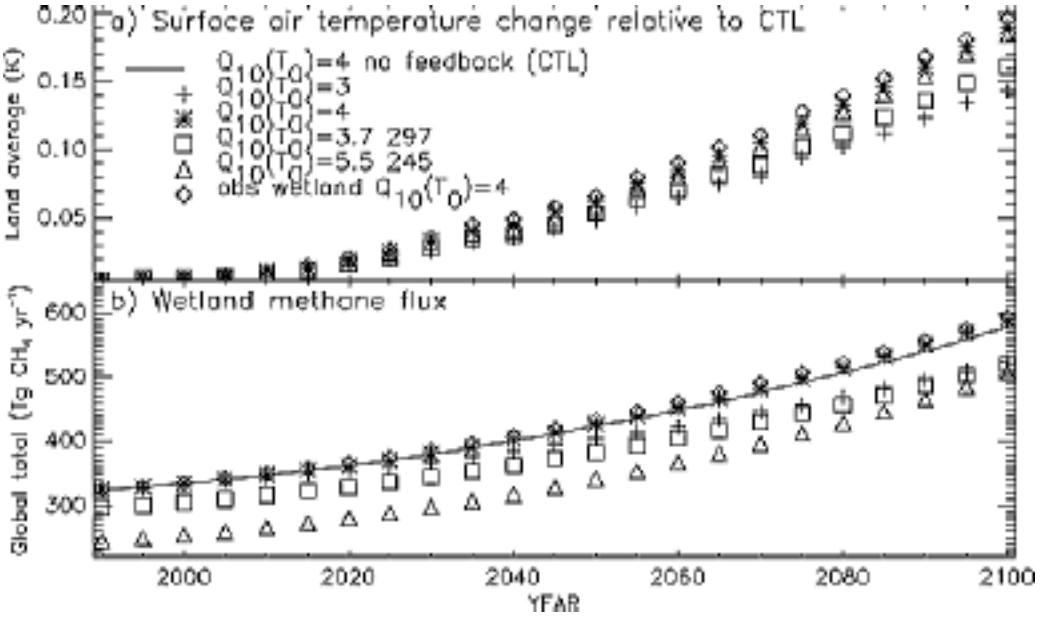


Figure 6. The variation in the methane flux from wetlands with changing climate [Gedney *et al.* 2004].

As well as being a source, ecosystems are also a sink for many trace gases through dry deposition to vegetation and soil [Wesley 1989]. The deposition velocities of species depend on the type of vegetation and soil, and also on meteorologically influenced parameters such as the leaf and soil moisture [Sanderson *et al*. 2003b]. One of the main routes for ozone deposition to the surface is uptake through plant stomata. Figure 7 shows a picture of a plant stomate. Uptake through plant stomata allows ozone to damage the cell membranes [Ashmore 2005].

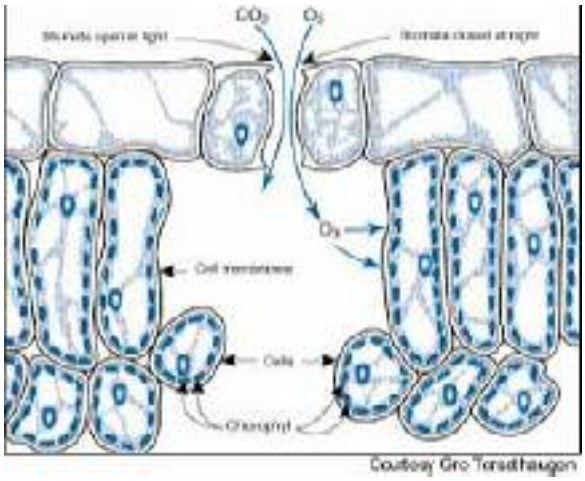


Figure 7. Diagram of a leaf surface, showing the stomatal opening.

The opening of plant stomata is determined by meteorological factors including the, the atmospheric concentration of CO_2 and the water stress of the plant. Plants open the stomata to take up CO_2 for photosynthesis, but restrict them to reduce water loss. Thus the degree of opening of the stomata is a balance between the CO_2 availability and water loss. Both these factors are likely to change in a future climate.

Sanderson *et al.* [2007] coupled an atmospheric chemistry model (STOCHEM) to the Met Office Hadley Centre climate model which includes a land surface exchange scheme to investigate the impact of changes in plant stomata on surface ozone concentrations. The focus was on the effect of changing the ambient CO_2 concentrations. With higher CO_2 concentrations, the plant's stomata can open less in order to get the same CO_2 flux. The modelling experiment consisted of two simulations, one with present day CO_2 and one with doubled CO_2. In the simulation with doubled CO_2 the meteorology was kept the same, only the chemical removal fluxes were allowed to respond to the increased CO_2. The impact on surface ozone of doubling CO_2 concentrations is shown in Figure 8. Ozone has increased globally. The largest changes are in the northern latitudes particularly in the northern spring.

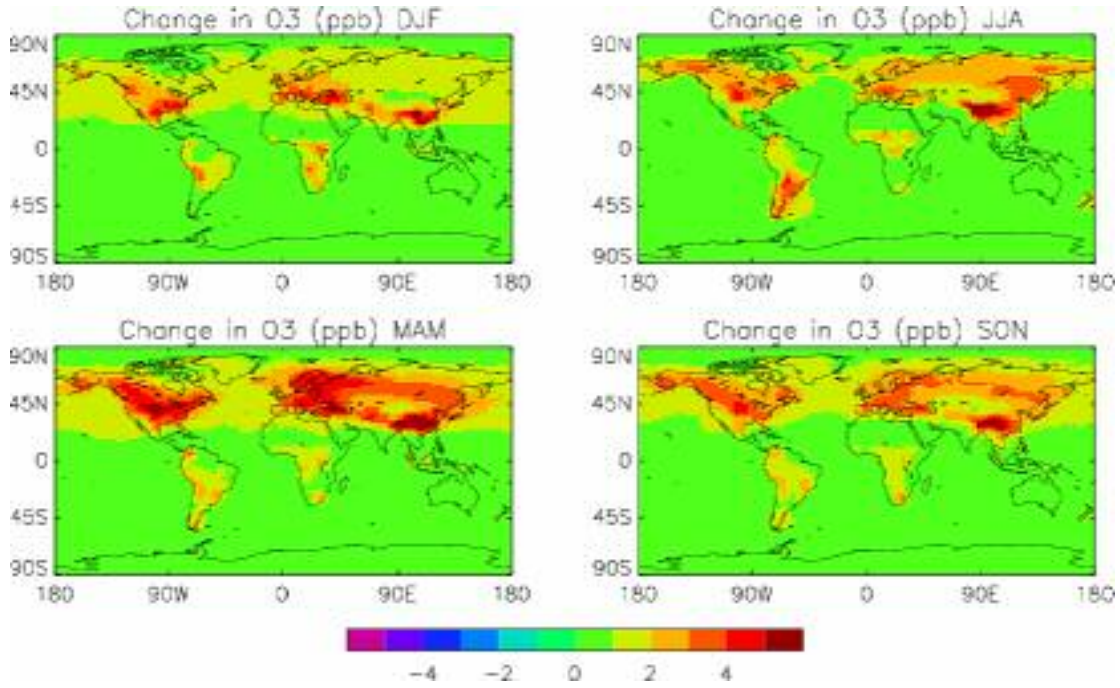


Figure 8. Changes in surface ozone concentration caused by the effect of doubling carbon dioxide concentrations on the stomatal removal. From Sanderson *et al* [2007].

Since ozone is both a human health pollutant and damaging to plants, it is instructive to assess the impact of CO_2 increases on both these factors. Figure 9 (top) shows the expected increase in springtime ozone over Europe due to the doubled CO_2 with consequent damaging implications for human health. Figure 9 (bottom) shows the change in the cumulative uptake of ozone by plant stomata for the same period. This is a useful measure of damage to plants [Ashmore 2005]. Although the surface concentrations rise under doubled CO_2 the plant damage halves.

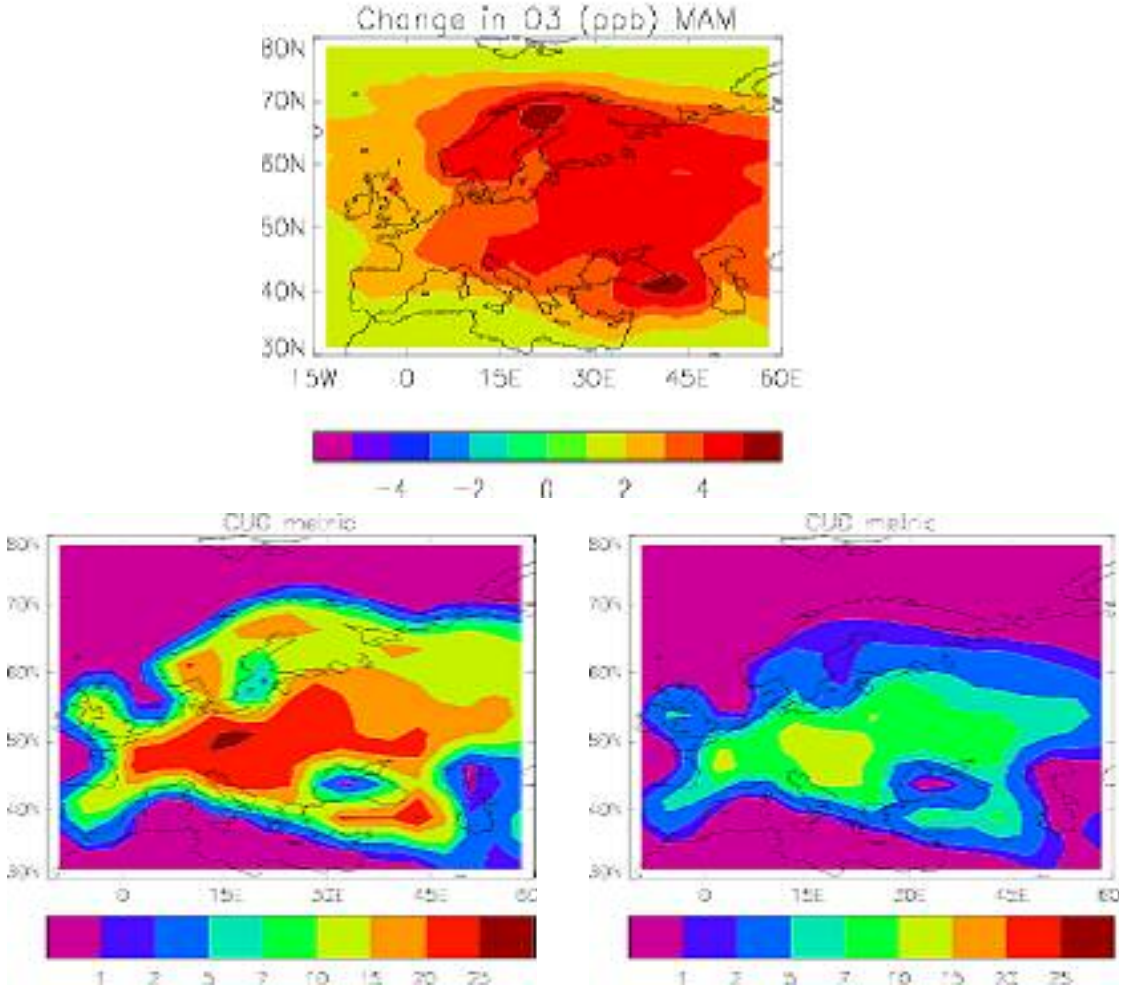


Figure 9. Top figure, change in surface ozone concentrations in ppb due to the effect of doubled CO_2 concentrations of the stomatal conductance. Lower left: The ozone damage metric Cumulative Uptake of Ozone (CUO) for present day CO_2 levels integrated over March-April-May, in mmol m^{-2}. Lower right: the same metric calculated for doubled CO_2 levels.

Plants also close their stomata in response to water stress. Therefore any increase in water stress in a changed climate may be expected to have a similar effect to the direct CO_2 impact. That is increasing surface ozone concentrations with associated human health consequences, but decreasing the ozone damage caused to plants. Plant damage metrics based purely on the surface ozone concentrations, such as AOT40, will increase with increasing CO_2, thus predicting the opposite sign of change. It is thus essential to use a metric reflecting the atmosphere-surface exchange of ozone.

The meteorological changes are not only likely to be important in a seasonally averaged sense, but are likely to be particularly important during pollution episodes, and have yet to be quantified. Vautard *et al.* [2005] found that a simulation of ozone in the August 2003 European heatwave was improved by assuming a doubling of the surface resistance to ozone deposition.

Conclusions

The net effect of climate change on the tropospheric ozone burden is still not well determined. It is expected that the continental surface concentrations will be effected by changes in the atmosphere-surface exchange of reactive gases. Important mechanisms by which atmosphere-surface exchange might by perturbed by climate change involve the biosphere. Here we have focussed on terrestrial vegetation. The oceanic ecosystems might also be affected by climate change, but their impacts on continental air quality are likely to be smaller.

Increases in natural emissions of ozone precursors such as isoprene and methane will make ozone pollution worse in future. Decreases in ozone removal by vegetation due to the direct effect of CO_2, and the indirect effect of CO_2 through changing climate will again increase ozone pollution levels but reduce the damage to plants (including crops).

Changes in the surface-atmosphere exchange of trace gases due to climate change will have an impact on ozone chemistry. These changes are likely to be heterogeneous, with significant increases in surface ozone concentrations in particular regions and less in others. Hence simulations of future air quality will need to take into account surface exchange processes in order to make reliable predictions for policy use. In order to do this, detailed maps of vegetation coverage and type will be required.

References

Aselmann, I. and P. Crutzen, Global distribution of natural freshwater wetlands and rice paddies, their net primary productivity, seasonality and possible methane emissions, *J. Atmos. Chem.*, **8**, 307– 358, 1989.

Ashmore, M. R., Assessing the future global impacts of ozone on vegetation. *Plant Cell Environ*. **28**, 949–964, 2005.

Butchart, N., and A. A. Scaife, Removal of chlorofluorocarbons by increased mass exchange between the stratosphere and troposphere in a changing climate, *Nature*, **410**, 799– 802, 2001.

Collins W. J., R. G. Derwent, B. Garnier, C. E. Johnson, M. G. Sanderson, D. S. Stevenson, Effect of stratosphere-troposphere exchange on the future tropospheric ozone trend, *J. Geophys. Res.*, **108** (D12), 8528, doi:10.1029/2002JD002617, 2003.

Cox, P. M., Betts, R. A., Jones, C. D., Spall, S. A. & Totterdell, I. J., Acceleration of global warming due to carbon-cycle feedbacks in a coupled climate model. *Nature* 408, 184–187, 2000.

Gedney, N., P.M. Cox and C. Huntingford, Climate feedback from wetland methane emissions, *Geophys. Res. Lett.* **31** (20), 2004.

Guenther, A., *et al.,* A global model of natural organic compound emissions, *J. Geophys. Res*., **100**, 8873– 8892, 1995.

Johnson, C. E., D. S. Stevenson, W. J. Collins, R. G. Derwent, Role of climate feedback on methane and ozone studied with a coupled Ocean-Atmosphere-Chemistry model, *Geophys. Res. Lett*., **28**(9), 1723-1726, 10.1029/2000GL011996, 2001.

Lee J.D. *et al*., Ozone photochemistry and elevated isoprene during the UK heatwave of august 2003. *Atmos. Env.* **40** 7598-7613, 2006.

Sanderson, M. G., Jones, C. D., Collins, W. J., Johnson, C. E. & Derwent, R. G., Effect of climate change on isoprene emissions and surface ozone levels. *Geophys. Res. Lett*. **30**, 1936, doi:10.1029/2003GL017642, 2003a.

Sanderson, M.G., W. J. Collins, R. G. Derwent and C. E. Johnson, Simulation of Global Hydrogen Levels Using a Lagrangian Three-Dimensional Model. *J. Atmos. Chem*., **46** (1), 2003b.

Sanderson, M.G., W. J. Collins, D. L. Hemming and R. A. Betts, Stomatal conductance changes due to increasing carbon dioxide levels: Projected impact on surface ozone levels. *Tellus* **50B** 401-411, 2007.

Sitch, S., P.M. Cox, W.J. Collins and C. Huntingford, Indirect radiative forcing of climate change through ozone effects on the land-carbon sink. *Nature* doi:10.1038/nature06059, 2007.

Stedman, J.R., The predicted number of air pollution related deaths in the UK during the August 2003 heatwave. *Atmos. Env.* **38** 1087-1090, 2004.

Stevenson D. S., *et al.*, Multimodel ensemble simulations of present-day and near-future tropospheric ozone, *J. Geophys. Res*., **111**, D08301, doi:10.1029/2005JD006338, 2006.

Stott, P.A., D.A. Stone and M.R. Allen, Human contribution to the European heatwave of 2003. *Nature* **432**, 610-614, 2004.

Sudo K., M. Takahashi, H. Akimoto, Future changes in stratosphere-troposphere exchange and their impacts on future tropospheric ozone simulations, *Geophys. Res. Lett.*, **30** (24), 2256, doi:10.1029/2003GL018526, 2003.

Vautard, R., C. Honore, M. Beekmann and L. Rouil, Simulation of ozone duing the August 2003 heat wave and emissions control scenarios. *Atmos Env*, **39** 2957-2967, 2005.

Wesley, M., Parameterizations of surface resistance to gaseous dry deposition in regional-scale numerical models. *Atmos. Env*. **23**, 1293-1304, 1989.

West. J.J. and A.M. Fiore, Management of tropospheric ozone by reducing methane emissions. *Environ. Sci. Technol.* **39** 4685-4691, 2005.

Yienger, J. J., and H. Levy II, Empirical model of global soil biogenic NOx emissions, *J. Geophys. Res.,* **100**, 11,447–11,464, 1995.

Zeng G., and J. A. Pyle, Changes in tropospheric ozone between 2000 and 2100 modelled in a chemistry-climate model, *Geophys. Res. Lett.*, **30** (7), 1392, doi:10.1029/2002GL01670, 2003.

Impact of Climate Change on SOA and their Precursors

Plenary lecture to ACCENT CCAQ: Group 3

Thorsten Hoffmann

Institut für Anorganische und Analytische Chemie, Johannes Gutenberg-University of Mainz, Duesbergweg 10-14, Mainz, Germany

Summary

As a result of chemical reactions of volatile organic compounds (VOCs) in the atmosphere, which are released in large quantities from anthropogenic and in even higher amounts from natural sources, the concentrations of a series of climatic relevant trace species are significantly affected. Beside their potential influence on the regional distribution of ozone, biogenic VOCs are known to represent important precursors for the formation of secondary organic aerosols (SOA). The whole process, starting from the emission of biogenic VOCs from plants followed by the formation and removal of organic aerosols, can be viewed as a specific part of the global carbon cycle between the biosphere and atmosphere. Motivated by the increased scientific interest in the impact of the future atmosphere on atmospheric composition and processes, this contribution attempts to elucidate the current state of knowledge about the potential influence of climate change on organic aerosol formation. Due to the large amounts emitted and several potential feedback mechanisms the focus lies on SOA formation from naturally released hydrocarbons.

Introduction

Atmospheric aerosols interact both directly and indirectly with the Earth's radiation budget and climate. As a direct effect, the aerosols scatter or absorb sunlight. As an indirect effect, aerosols in the lower atmosphere can modify number and size of cloud droplets, changing how the clouds reflect and absorb sunlight, thereby affecting the Earth's radiation budget. Aerosols also can act as sites for chemical reactions to take place (heterogeneous chemistry). Hence, they play an important role in global climate and atmospheric chemistry. Furthermore, atmospheric aerosols affect our environment at the local and regional levels. Aerosols are now becoming recognised as a significant health problem, especially in regard to respiratory diseases.

The formation of organic aerosols from the oxidation of hydrocarbons is only one but an important contribution to the overall composition of atmospheric aerosols. One major pathway leading to organic aerosols formation in the atmosphere is gas-to-particle conversion. In general, the volatile aerosol precursors are first decomposed in the gas phase by bimolecular reactions or photolysis followed by the formation of products with a lower volatility. Higher functionalised compounds with hydroxyl, carbonyl, carboxyl groups or groups containing heteroatoms are formed in an oxidising environment, which will either condense on existing particles or even form new aerosol particles. To distinguish this fraction of tropospheric aerosols from the direct input of particulate organics into the atmosphere it is specified as secondary organic aerosol (SOA).

Historical

The optical effects of atmospheric aerosol particles formed from the oxidation of VOCs were recognised quite early by humans. Sha-co-na-qe "Place of Blue Smoke" was the name given for the Great Smoky Mountains by the Cherokee Indians, of course without knowing the cause of the haziness often observed in the summertime above the forested Appalachian Highlands. This phenomenon of forested regions – that they are frequently enveloped in a blue haze or smoke – is induced by Rayleigh scattering of submicrometer particles. Numerous other forested mountain sites are named after this phenomenon: 'Blue Mountains', 'Blue Ridges' or 'Smoky Mountains' can be found for example in India close to the Burman border, in Jamaica, at the east coast of Australia (Figure 1) and even several times in North America (Montana, Oregon, Idaho, Maine, Pennsylvania, Tennessee).

Figure 1. Biogenic secondary aerosol formation (blue haze), Blue Mountains, Australia.

The first connection between volatile organic compounds and the formation of atmospheric particles was probably made by Arie Haagen-Smit at Caltech in 1952 in a strongly anthropogenically influenced environment. Studying various aspects of the Los Angeles smog formation he not only explained ozone and peroxide formation by the photochemistry of the released hydrocarbons and nitrogen oxides but also connected the decrease in visibility during smog episodes to the condensation of aldehydes and acids formed in the oxidation the hydrocarbons. In 1960 F.W. Went, director of the Missouri Botanical Garden and former colleague of Haagen-Smit at Caltech, published an extensive article in Nature titled 'Blue hazes in the atmosphere'. Based on his observations staying at a countryside site and everyday experiences as well as his knowledge about secondary plant products, he finally also connected the occurrence of the natural phenomena with the volatilisation and gas phase oxidation of terpenes from terrestrial vegetation.

However, during these first years of atmospheric chemistry and the following decades the main interest in the VOC chemistry was focused on gas-phase photochemistry. About 1990 more and more interest was developed to understand also the aerosol formation behaviour of hydrocarbons, driven by the awareness of the role of natural and anthropogenic aerosols in the radiative properties of the atmosphere and the Earth's climate. Moreover, the ozone hole research in the Antarctic clearly showed that heterogeneous reactions on surfaces of air suspended matter can also influence gas phase composition. Another major driver to investigate the origin and formation of aerosol particles in the last decades is their effect on human health. It has been shown that cardio-pulmonary diseases and mortality are related to the presence of fine

particulate matter [Dockery *et al.,* 1993; Laden *et al.,* 2000; Mar *et al.,* 2000; Tsai *et al.,* 2000]. As a consequence of the increased scientific interest new instrumental techniques for particle analysis have been developed at a rapid rate in an effort to produce methods with lower detection limits, shorter temporal resolution, and increased selectivity with the goal of increasing our understanding of atmospheric processes. Especially mass spectrometric on-line techniques have been developed during the last years [Sipin *et al.,* 2003].

Sources and sinks of atmospheric particles

As mentioned above, particles in the atmosphere are often divided into primary and secondary particles according to their formation processes. Primary particles are released directly into the atmosphere whereas secondary particles are produced within the atmosphere as a consequence of the conversion of volatile precursors into low or non-volatile substances. Formation processes of primary particles are basically mechanical production (abrasion, suspension and sea spray) and production during combustion processes (condensation of hot vapours or formation inside flames (*e.g.* soot particles)) [Seinfeld and Pandis, 1998]. In general, mechanical processes create coarse particles (diameter >1 μm or >2.5 μm depending on the definition or available sampling methods) whereas combustion processes create fine particles which might coagulate right after production (*e.g.* chain aggregates of soot particles). Secondary atmospheric particles belong to the fine particle fraction and they are created by the so called "nucleation process". The nucleation process in the troposphere is currently not completely understood and several mechanisms are discussed [Kulmala, 2003]. One hypothesis about new particle production in the atmosphere assumes that the process is initialised by the formation of sulfuric acid containing clusters (thermodynamically stable clusters) in the size range of 1 nm which grow under suitable conditions, for example, the availability of condensable vapours, into a size range of 3 to 20 nm, the so-called nucleation mode. If the concentration of condensable vapours is not high enough, the clusters will be rapidly lost by coagulation and no new particles will be formed. However, once formed the nucleation mode particles can continue to grow by uptake of condensable vapours into the Aitken mode (around 20 to 100 nm) and further to particles in the accumulation mode (100 nm range) [Kulmala *et al.,* 2004]. Condensable vapours mean low volatile compounds which are produced during chemical reactions in the atmosphere from volatile precursors. Due to the Kelvin effect (smaller droplets have higher vapour pressures) these vapours cannot condense without a condensation nuclei (*e.g.* a cluster). Condensable vapours might be inorganic like sulfuric acid or organic like low volatile products from the terpene oxidation. These low volatile compounds are not only involved in the formation or growth of secondary particles but they can also condense onto pre-existing particles leading to increased particle size and mass and to an alteration of the chemical composition which might also alter the physical or physicochemical properties (light scattering, hygroscopicity, *etc.*) which affect the influence of aerosols on climate.

Processes which act as sinks of atmospheric particles are dependent on the particle sizes. Coarse particles are being removed mainly by dry deposition (sedimentation). Particles in the accumulation mode are being eliminated mostly by wet deposition (rainout, washout). The main sink for smaller particles (Aitken and nucleation mode) is coagulation with other particles.

Sources and composition of secondary organic aerosols

Secondary organic aerosols (SOAs) are produced (1) mainly by gas-phase oxidation of volatile organic compounds that can either form new particles or condense onto pre-existing particles, (2) by heterogeneous reactions on particle surfaces or (3) by in-cloud processing. Precursors of organic SOA are mostly volatile reactive biogenic (*e.g.* terpenes) or anthropogenic (*e.g.* aromatics) hydrocarbons. The dominant loss processes for volatile organic compounds in the troposphere are chemical transformations by reaction with hydroxyl radicals (OH), nitrate radicals (NO_3) and ozone. Especially for the oxidation of the mostly unsaturated biogenic hydrocarbons, all three of these reactions must be considered in assessing the transformation processes of a given alkene. Figure 2 shows a general reaction scheme for the oxidation of two VOCs, mesitylene (a typical anthropogenic VOC) and α-pinene (one of the most important natural VOCs). All three reactions lead to the formation of short-living organic radicals, which rearrange, decompose or react further with other atmospheric constituents. A fraction of the products stay in the gas-phase (*e.g.* formaldehyde, glyoxal, acetone) and influence important tropospheric processes, such as ozone formation. Some of these volatile products (*e.g.* glyoxal) might be taken up on a longer time scale in the condensed phase and undergo aerosol chemical processing (see below). Furthermore, higher molecular weight products are generated from VOC oxidation, some semi-volatile compounds, such as carbonyls or alcohols, some low-volatile products, such as diacids. Due to their semi-volatile or even low-volatile character these products can instantaneously contribute to the particle phase (gas/particle partitioning) or even form new particles by homogeneous nucleation.

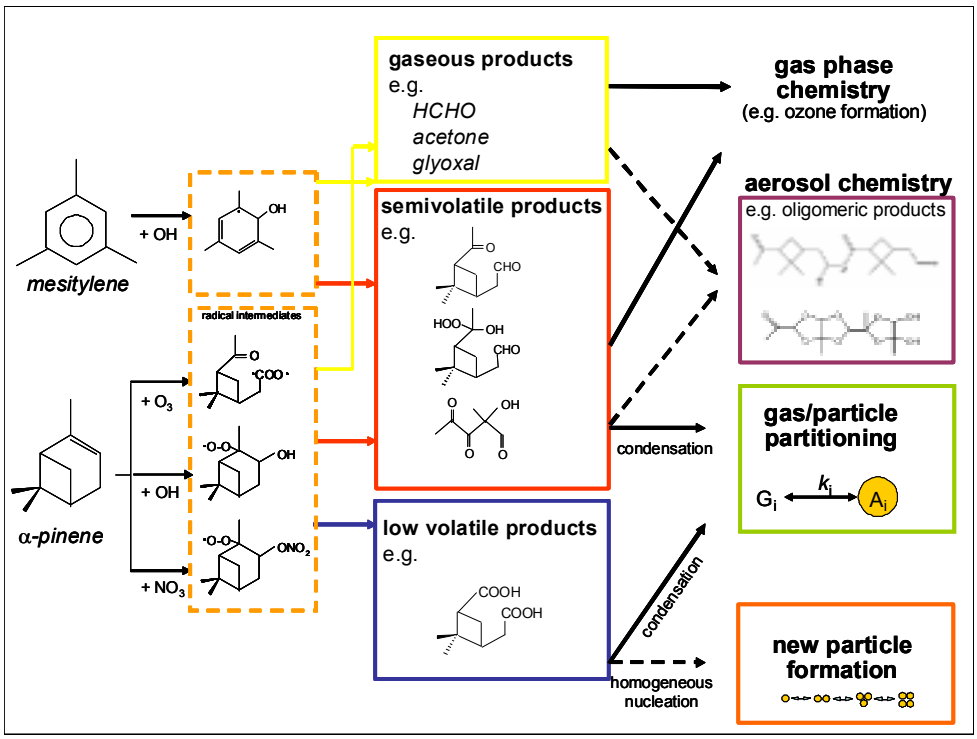


Figure 2. Mechansims leading to gaseous or condensable species from anthropogenic (*e.g.* mesitylene) and biogenic (*e.g.* α-pinene) precursors and some important subsequent processes.

This gas-particle partitioning of semi-volatile (and also low-volatile) compounds can be described by gas-particle partitioning models introduced by [Pankow 1994; Odum *et al.,* 1996]. These models consider the dependence of the concentration of an individual organic compound *i* in the particle phase from the available absorbing organic aerosol mass (MO), the partitioning coefficient of compound *i* and the concentration of *i* in the gas phase:

$$c_{aer} = c_{gas} * K_{om} * MO$$

where K_{om}: partitioning coefficient of *i* ($m^3/\mu g$) (temperature dependent)
c_{aer}: concentration of compound *i* in the absorbing organic particle phase (ng/m^3)
c_{gas}: concentration of *i* in the gas phase (ng/m^3)
MO: concentration of the absorbing organic phase in the aerosol ($\mu g/m^3$)

Biogenic SOA

Precursors of biogenic SOA in the continental environment are mainly unsaturated hydrocarbons namely (mono-) terpenes, sesquiterpenes and isoprene. The SOA-forming potential of terpenes is well known and was intensively investigated [Went 1960; Zhang *et al.,* 1992; Hoffmann *et al.,* 1997; Hoffmann *et al.,* 1998; Kavouras *et al.,* 1998; Griffin *et al.,* 1999; Yu *et al.,* 1999; O'Dowd *et al.,* 2002], whereas isoprene was only most recently found to form low volatile secondary products [Claeys *et al.,* 2004; Claeys *et al.,* 2004].

Today several evidences exits that forests are a substantial source of both aerosol mass and aerosol number. These investigations supply a straightforward relation between emissions of monoterpenes and gas-to-particle formation over regions substantially lacking in anthropogenic aerosol sources. As a consequence forests have to be regarded as important contributors to aerosol mass and number [Tunved *et al.,* 2006].

The future atmosphere and SOA formation

Emission of natural SOA precursors

This clear connection between biogenic VOC release and the formation of aerosol mass and number is a first obvious implication of the effect of the future atmosphere and climate on SOA formation. Due to the strong temperature dependence of the emission rate of natural VOCs from forest trees, an increasing global average temperature will increase the aerosol precursor emission and consequently probably also the aerosol concentration. In principle, it is also possible that the increasing global CO_2 concentration will influence the VOC emission rate, although the direction and magnitude of this effect is much less clear. Based on this interactions Kulmala and coworkers suggested a possible feedback loop: Considering that globally increasing temperatures and CO_2 fertilisation are likely to lead to increased photosynthesis and forest growth, an increase in forest biomass would increase emissions of non-methane biogenic volatile organic compounds and thereby enhance organic aerosol production [Kulmala *et al.,*, 2004, Tunved *et al.,* 2006], which in turn will affect global radiation balance due to the increase in CCN number concentration.

Temperature influence on gas-particle partitioning

The gas-particle partitioning of semi-volatile and low-volatile compounds contains another direct connection between future climate and SOA formation. The temperature dependence of the partitioning coefficient [Takekawa *et al.,* 2003] of the individual particle forming compounds would decrease the amount of SOA formed in a warmer climate. Due to the high relative contribution of biogenic SOA again this influence can

be expected to be especially important for natural SOA formation. However, recent measurements indicate that this influence of temperature on the SOA yield is quite weak, especially at temperatures above 15 °C and at ambient concentration levels [Pathak *et al.*, 2007].

SOA and gas phase chemistry

Figure 2 shows the different oxidation pathways for biogenic VOCs. Since the individual products and the product distribution from the three individual oxidation reactions are quite different, the SOA yields from the particular oxidation reactions can also be expected to be different. However, the lack of detailed knowledge about the individual products still complicates the assessment of biogenic SOA formation under ambient conditions. Especially the gas-phase ozonolysis was investigated in detail in the past. Their low vapour pressure (or large absorption equilibrium constant K) govern a substantial fraction of the ozonolysis products into the particle phase. Less is known about the product formation of the two other relevant oxidation pathways under tropospheric conditions, namely the OH and NO_3 initiated VOC degradation. While numerous gas-phase products could be identified, especially in the case of OH reactions, the significance of the two oxidants in terms of aerosol formation in the ambient atmosphere is still not sufficiently known. This is because difficulties arise when these oxidation pathways are investigated in environmental simulation chambers. Most chamber experiments are still made in the presence of relatively high levels of NO_x, which heavily influence the chemistry of intermediate species (*e.g.* organic peroxy radicals) [Keywood *et al.*, 2004; Docherty and Ziemann, 2003]. In the remote or tropical atmosphere, where NO_x concentrations are in the ppt range, permutation reactions of these radicals gain importance, presumably causing a different product distribution and aerosol yields. In general, the available information indicate that beside ozonolysis the reaction of biogenics with NO_3-radicals represent an efficient route to the formation of condensable products, an observation that could be relevant for the night-time chemistry in forested areas. Tropospheric lifetimes of biogenic hydrocarbons with respect to their reaction with NO_3 can lie in the order of minutes, hence could represent an important degradation pathway if NO_3 is available. Whether or not the high aerosol yields observed in smog chamber experiments hold under typical ambient conditions has to be elucidated in the future. However, based on the available experimental data, Kanakidou *et al.* suggest an increase from 17-28 Tg/yr global biogenic SOA production in preindustrial times to 61-79 Tg/yr at present (about 300 % increase) mainly due to increased ozone concentrations, NO_x (NO_3) and emission of POA [Kanakidou *et al.*, 2000]

SOA and aerosol chemistry

More recent studies show that also volatile carbonylic products formed in the gas phase oxidation of organics may contribute over a longer period of time to the SOA mass by the formation of low volatile oligomers, for example via acid catalysed reactions of aldehydes or ketones on the particle surfaces or inside the particles (aldol reaction/condensation, acetal formation). These processes result in increased particle mass and a lower volatility. This might be the case for both biogenic and anthropogenic precursors [Jang *et al.,* 2002; Jang *et al.,* 2004; Kalberer *et al.,* 2004]. There are also evidences for the direct formation of oligomeric products by heterogeneous reactions of unsaturated gas phase compounds (*e.g.* isoprene) on particle surfaces [Limbeck *et al.,* 2003]. Several groups speculate that these oligomeric products formed from gaseous precursors could represent a substantial fraction of the so-called “humic like substances” (HULIS) often identified in atmospheric aerosols. HULIS is a collective

term for an on the molecular level unidentified group of particle phase compounds, which add to the water soluble organic carbon.

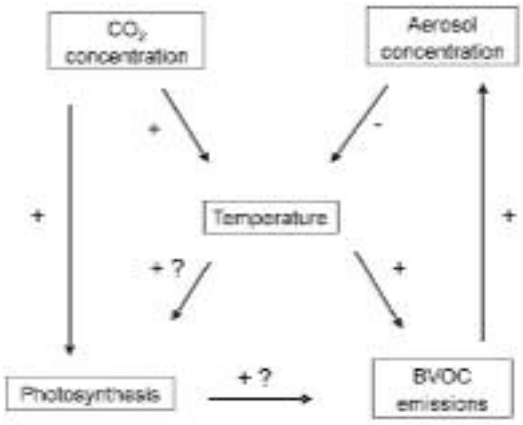


Figure 3. A feedback mechanism linking forests, aerosols, and climate [Tunved *et al.*, 2006, Kulmala *et al.*, 2004].

This generation of new particle phase products from gas phase constituents during the atmospheric lifetime of aerosols is part of the so-called atmospheric ageing of organic particles, a process that is currently not well characterised. Beside the incorporation of reactive gas phase species into the organic aerosol fraction by oligomer formation, ageing also includes the degradation or chemical modification of particle phase constituents by atmospheric oxidants. Since these chemical modifications will result in alterations of the physical (volatility, light absorption, light scattering) and physico-chemical properties (water solubility, CCN-activity) of atmospheric aerosols, the investigation of these processes have to be addressed in future research on organic aerosols.

Consequently several open questions in connection with the future atmosphere and the effects on aerosol chemistry remain. Certainly the topic contains several potential anthropogenic influences, such as influence of aerosol acidity or tropospheric oxidation capacity. For example, it is unclear which of the different processes involved (*i.e.* oligomerization – oxidative processing) will dominate the properties of the organic particles (incl. SOA) in the troposphere (*e.g.* increase or decrease of hygroscopicity of OA).

SOA modelling

The incorporation of SOA formation into atmospheric models is not an easy task since a variety of chemical and physico-chemical processes influence the SOA particle mass in the ambient atmosphere. A sensitivity analysis of SOA production and transport modelling [Tsigaridis and Kanakidou 2003] showed a factor of about 20 of uncertainty in predicting the SOA production considering the different influences of partitioning and ageing, excluding (!) the uncertainties of precursor emissions and individual oxidation pathways. This results in an annual global production of SOA from 2.55 to 47.12 Tg of organic matter per year. Another study showed a difference of SOA production between using the partitioning method and the bulk yield method (ignoring the partitioning mechanism) of 15.3 and 24.6 Tg per year [Lack *et al.,* 2004]. Therefore, the existing uncertainties to quantitatively understand the individual contributions to SOA formation complicate the goal to include SOA formation into global modelling approaches and predict future developments. This is especially true for tropical regions, since not only most of the VOCs are released into the boundary layer in these regions, but also rapid changes in the emission strength can be expected in the future. Another

challenge of SOA modelling will be the incorporation of aerosol chemistry into aerosol modelling approaches (*i.e.* also considering the effect of atmospheric composition change on ageing).

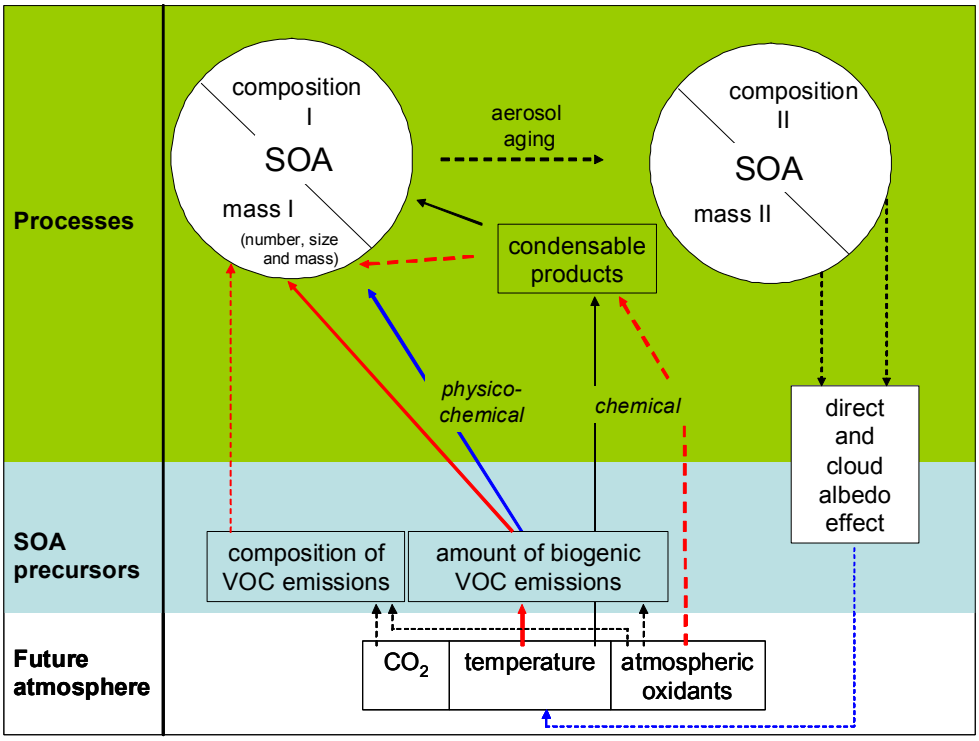


Figure 4. Potential impact of the future atmosphere (CO_2-level, temperature, concentration of oxidants) on precursor emission and SOA formation (red arrows = increasing, blue arrows = decreasing, black arrows = unclear direction, solid arrows = high level of understanding, dotted arrows = low level of understanding).

Conclusions

Figure 4 shows the various potential connections between the parameters involved in SOA formation, especially natural SOA formation. The most important factors that can be expected to change in a future climate and influence SOA formation are the temperature, the CO_2 concentration and the concentration of oxidants. Ignoring land use change - obviously another important parameter for the emission of aerosol precursors - an increasing temperature will increase the release of biogenic VOCs, thereby increasing the production of aerosol mass. On the other hand at higher temperatures the vapour pressures of the condensable products are higher, reducing the amount of SOA. However, as mentioned above there exist indications that the latter effect is less pronounced at ambient concentrations and in typical temperatures regimes. In case that the higher precursor emission rate at higher temperatures over-compensates the increased vapour pressures of the products, possibly also the number concentration of tropospheric aerosol particles from natural sources could finally be enlarged. Much less clear is the influence of atmospheric composition change (*e.g.* elevated CO_2 concentration, increased oxidative stress) on the composition of plant emissions. If for example higher amounts of sesquiterpenes or other compounds with a high aerosol formation potential are emitted under these conditions [Heiden *et al.*, 1999, Beauchamp *et al.*, 2005] another pathway for the formation of higher SOA masses would be the consequence. From the current understanding of changing atmospheric oxidant levels (*e.g.* higher tropospheric ozone levels) and their effects on SOA formation, also an

increased formation of SOA mass can be expected. However, the different reaction pathways also alter the chemical composition of the aerosol particles. Finally, a very diffuse knowledge exists about the effect of atmospheric composition change on the ageing process of atmospheric particles and the consequences for their ability to act as CCN.

References

Beauchamp J., A. Wisthaler, A. Hansel, E. Kleist, M. Miebach, U. Niinemets, U. Schurr and J. Wildt, Ozone induced emissions of biogenic VOC from tobacco: relationships between ozone uptake and emission of LOX products more options, *Plant cell and environ.,* **28(10)** (2005) 1334-1343.

Claeys, M., W. Wang, A.C. Ion, I. Kourtchev, A. Gelencser and W. Maenhaut, Formation of secondary organic aerosols from isoprene and its gas-phase oxidation products through reaction with hydrogen peroxide, *Atmos. Environ.,* **38(25)** (2004) 4093-4098.

Claeys, M., B. Graham, G. Vas, W. Wang, R. Vermeylen, V. Pashynska, J. Cafmeyer, P. Guyon, M.O. Andreae, P. Artaxo and W. Maenhaut, Formation of secondary organic aerosols through photooxidation of isoprene, *Science,* **303(5661)** (2004) 1173-1176.

Docherty K.S. and P.J. Ziemann, Effects of stabilized Criegee intermediate and OH radical scavengers on aerosol formation from reactions of beta-pinene with O3, *Aerosol. Sci. and Techn.,* **37(11)** (2003) 877-891.

Dockery, D.W., C.A. Pope, X. Xu, J. Spengler, J.H. Ware, M.E. Fay, B.G. Ferris and F.E. Speizer, An association between air pollution and mortality in six US cities, *New England J. Medicine,* **329** (1993) 1753-1759.

Griffin, R.J., D.R. Cocker III, J.H. Seinfeld and D. Dabdub, Esitmate of global atmospheric organic aerosol from oxidation of biogenic hydrocarbons, *Geophys. Res. Lett.,* **26** (1999) 2721-2724.

Heiden A.C., T. Hoffmann, J. Kahl, Emission of volatile organic compounds from ozone-exposed plants, *Ecological Applications*, **9(4)** (1999) 1160-1167.

Hoffmann, T., R. Bandur, U. Marggraf and M. Linscheid, Molecular composition of organic aerosols formed in the alpha- pinene/O-3 reaction: Implications for new particle formation processes, *J. Geophys. Res.,* **103(D19)** (1998) 25569-25578.

Hoffmann, T., J.R. Odum, F. Bowman, D. Collins, D. Klockow, R.C. Flagan and J.H. Seinfeld, Formation of organic aerosols from the oxidation of biogenic hydrocarbons. *J. Atmos. Chem.,* **26(2)** (1997) 189-222.

Jang, M.S., N.M. Czoschke, S. Lee and R.M. Kamens, Heterogeneous atmospheric aerosol production by acid-catalyzed particle-phase reactions, *Science,* **298(5594)** (2004) 814-817.

Jang, M., N.M. Czoschke and A.L. Northcross, Atmospheric organic aerosol production by heterogeneous acid-catalyzed reactions, *Chemphyschem.,* **5(11)** (2004) 1647-1661.

Kalberer, M., D. Paulsen, M. Sax, M. Steinbacher, J. Dommen, A.S.H. Prevot, R. Fisseha, E. Weingartner, V. Frankevich, R. Zenobi and U. Baltensperger, Identification of polymers as major components of atmospheric organic aerosols, *Science,* **303(5664)** (2004) 1659-1662.

Kanakidou M., K. Tsigaridis, F.J. Dentener and P.J. Crutzen, Human-activity-enhanced formation of organic aerosols by biogenic hydrocarbon oxidation, *J. Geophys. Research-Atmos.*, **105(D7)** (2000) 9243-9254.

Kavouras, I.G., N. Mihalopoulos and E.G. Stephanou, Formation of atmospheric particles from organic acids produced by forests, *Nature*, **395** (1998) 683-686.

Keywood M.D., J.H. Kroll, V. Varutbangkul; R. Bahreini, R.C. Flagan and J.H. Seinfeld, Secondary organic aerosol formation from cyclohexene ozonolysis: Effect of OH scavenger and the role of radical chemistry, *Environ. Sci. & Techn.,* **38(12)** (2004) 3343-3350.

Kulmala, M., How particles nucleate and grow, *Science*, **302(5647)** (2003) 1000-1001.

Kulmala, M., H. Vehkamaki, T. Petajda, M. Dal Maso, A. Lauri, V.M. Kerminen, W. Birmili and P.H. McMurry, Formation and growth rates of ultrafine atmospheric particles: a review of observations, *J. of Aerosol Sci.*, **35(2)** (2004) 143-176.

Kulmala, M., T. Suni, K.E.J. Lehtinen, M. Dal Maso, M. Boy, A. Reissell, U. Rannik, P. Aalto, P. Keronen, H. Hakola, J. Bäck, T. Hoffmann, T. Vesala, and P. Hari, A new feedback mechanism linking forests, aerosols, and climate, *Atmos. Chem. and Phys.*, **4** (2004) 557–562.

Lack, D.A., X.X. Tie, N.D. Bofinger, A.N. Wiegand and S. Madronich, Seasonal variability of secondary organic aerosol: A global modeling study, *J. of Geophys. Research-Atmos.*, **109(3)** (2004) D03203 doi:10.1029/2003JD003418.

Laden, F., L.M. Neas, D.W. Dockery and J. Schwartz, Association of fine particulate matter from different sources with daily mortality in six US cities, *Environ. Health Perspectives,* **108(10)** (2000) 941.

Limbeck, A., M. Kulmala and H. Puxbaum, Secondary organic aerosol formation in the atmosphere via heterogeneous reaction of gaseous isoprene on acidic particles - art. no. 1996, *Geophys.Res.Lett.,* **30(19)** (2003) 1996-1996.

Mar, T.F., G.A. Norris, J.Q. Koenig and T.V. Larson, Associations between air pollution and mortality in Phoenix, 1995-1997, *Environ. Health Perspectives*, **108(4)** (2000) 347.

O'Dowd, C.D., P. Aalto, K. Hameri, M. Kulmala and T. Hoffmann, Aerosol formation - Atmospheric particles from organic vapours, *Nature* **416(6880)** (2002) 497-498.

Odum, J.R., T. Hoffmann, F. Bowman, D. Collins, R.C. Flagan and J.H. Seinfeld, Gas/particle partitioning and secondary aerosol formation, *Environ. Sci. Technol.,* **30** (1996) 2580-2585.

Pankow, J.F., An absortion model of gas/particle partitioning of organic compounds in the atmosphere, A*tmos. Environ*., **28(2)** (1994) 185-188.

Pankow, J.F., An absortion model of the gas/aerosol partitioning involved in the formation of secondary organic aerosol, *Atmos. Environ.*, **28(2)** (1994) 189-193.

Pathak, R.K., C.O. Stanier, N.M. Donahue and S.N. Pandis, Ozonolysis of a-pinene at atmospherically relevant concentrations: Temperature dependence of aerosol mass fractions (yields), *J. of Geophys. Research*, **112** (2007) D03201, doi:10.1029/2006JD007436.

Seinfeld, J.H. and S.N. Pandis, 1998, *Atmospheric chemistry and physics*. John Wiley & Sons, Inc., ISBN 0-471-17815-2.

Sipin, M.F., S.A. Guazzotti and K.A. Prather, Recent advances and some remaining challenges in analytical chemistry of the atmosphere, *Anal. Chem.*, **75(12)** (2003) 2929-2940.

Takekawa, H., H. Minoura and S. Yamazaki, Temperature dependence of secondary organic aerosol formation by photo-oxidation of hydrocarbons, *Atmos. Environ.,* **37** (2003) 3413-3424.

Tsai, F.C., M.G. Apte and J.M. Daisey, An exploratory analysis of the relationship between mortality and the chemical composition of airborne particulate matter, *Inhalation Toxicology,* **12** (2000) 121.

Tsigaridis K., M. Krol, F.J. Dentener, Y. Balkanski, J. Lathiere, S. Metzger, D.A. Hauglustaine and M. Kanakidou, Change in global aerosol composition since preindustrial times, *Atmos. Chem. and Phys.*, **6** (2006) 5143-5162.

Tsigaridis, K. and M. Kanakidou, Global modelling of secondary organic aerosol in the troposphere: a sensitivity analysis, *Atmos. Chem. and Phys.,* **3** (2003) 1849-1869.

Tunved, P., H.-C. Hansson, V.-M. Kerminen, J. Ström, M. Dal Maso, H. Lihavainen, Y. Viisanen, P.P. Aalto, M. Komppula and M. Kulmala, High Natural Aerosol Loading over Boreal Forests, *Science*, **312** (2006) 262-263.

Went, F.W., Blue hazes in the atmosphere, *Nature,* **187** (1960) 641-643.

Yu, J.Z., D.R. Cocker, R.J. Griffin, R.C. Flagan and J.H. Seinfeld, Gas-phase ozone oxidation of monoterpenes: Gaseous and particulate products, *J. Atmos. Chem.,* **34(2)** (1999) 207-258.

Zhang, S.H., M. Shaw, J.H. Seinfeld and R.C. Flagan, Photochemical Aerosol Formation from alpha-Pinene- and beta- Pinene, *J. Geophys. Res.,* **97(D18)** (1992) 20717-20729.

Impact of Climate Change on Air Quality: Building Observations and Modelling Systems

Plenary lecture to ACCENT CCAQ: Group 4

Øystein Hov

EMEP Meteorological Synthesizing Centre West, Norwegian Meteorologial Institute, PO Box 43, NO-0313 Oslo, Norway.
Also at Department of Geosciences, University of Oslo, Norway.

Science issues

There are two-ways links between changes in short lived greenhouse gas and particulate matter emissions/concentrations and climate change. There are many feedbacks from climate change on air quality (sulfur, nitrogen, volatile organic compounds, secondary species, heavy metals and persistent organic pollutants). Over the next 1-2 decades it is expected that natural variability will dominate over or be comparable to the climate change feedback on air quality. Thereafter the climate change signals will move the probability density functions (PDFs) for the values of parameters that control key processes for atmospheric chemical composition outside of currently known ranges.

An important challenge in observations and modelling is to identify the shape of the PDFs of parameters that control key processes for atmospheric chemical composition for current and past conditions, and to investigate what they may look like in the future. Reanalysis, using all available observations together with high resolution atmospheric models (NWP, CTM, coupled NWP + CTM), is an important tool to reassess the PDFs of parameters that control key processes for atmospheric chemical composition. This is a basis for the discussion of how climate change may impact on the atmospheric composition in the future.

Other important issues to resolve

Are changes in air quality arising from emission control measures larger than or less than the changes in air quality that may arise from climate change? Will regional emission changes affect regional climate? Will air quality emission reduction policies lead to emission changes that counteract climate change policies?

Links between changes in short lived greenhouse gas and particulate matter emissions/concentrations and climate change (both ways) need to be studied.

Critical processes for air quality are determined by the structure of the planetary boundary layer. Stable planetary boundary layers are of particular significance in air quality and they are not a main concern in regional or global climate models or even numerical prediction models.

Climatological observations done by the meteorological services and air quality observations done by environmental agencies/institutions) are separated, and this is counterproductive for the assessment of climate change/variability and air quality relationships. Some meteorological agencies like the Chinese Meteorological Agency now reorganise meteorological observations to merge with air quality observations.

Particulate matter and ozone impact on local precipitation and surface temperature. There is an under-exploitation of observed climate variability-air quality-relationships in the past as a training material for possible relationships between air climate and climate in the future.

Ozone and particulate matter redistribution affects synoptic weather patterns, gradients in radiative forcing created by tropospheric particles and ozone will modify synoptic weather patterns. For example, the Indian monsoon system modified by regional PM.

One should explore the observations further: *e.g.* identify how particulate matter may impact on precipitation (local); integrate air quality-observations and meteorological observations to merge the information and evaluation capabilities.

One should use climatological observations to underpin air quality-climate change relationships (*e.g.* use the 40 years of global reanalysis data from ECMWF (ERA40 (1961-2001) to identify the impact of meteorological variability on air quality variability/trends)

Feedback from climate change on air quality (sulfur, nitrogen, volatile organic compounds, secondary species, heavy metals and persistent organic pollutants)

There is evidence that trends in meteorological parameters due to climate change have an impact on air quality. Studies are being produced, but solid quantification of these processes is still lacking. The main meteorological parameters which will be affected are temperature, precipitation regimes; wind patterns. Changes in these parameters will have first order effects on processes such as natural (*e.g.* sea salt) and biogenic (*e.g.* volatile organic carbon) emissions, removal rates of chemicals, transport processes, and atmospheric chemistry (*e.g.* oxidising capacity). A wide range of secondary effects are also expected which will affect all major biogeochemical cycles. Also feedbacks on the climate system itself are to be expected. Adaptation measurements will also affect the whole loop.

It is recommended to implement monitoring and past data acquisition strategies to ensure comparable data-bases for analysis and interpretation. Methodologies which can be proposed to tackle these issues are twofold: off-line or on-line approaches, and include reanalysis of past meteorological data in connection with air quality (past data only), regional climate model ensembles linked to air quality (past and future data), and fully coupled climate-air quality models

Will natural variability dominate over climate change feedback on air quality in the coming decades?

Based on model simulations using observed climate (ERA40), ozone concentrations in Europe vary up ~ 5 % (relative to the standard deviation of the annual mean concentrations) due to variability in meteorology during 1979 to 2001. The year to year variability in annual ozone between 1979 and 2001 is −10 % to + 10 %, in the extreme case, 2003, shows + 20 % and some grid values over 30 %. Secondary inorganic aerosol variability is 5−30 %. Year to year variability is larger (> 20 %).

Ozone trends are −5 to +5 % per decade (1979−2001) in different parts of Europe. Secondary inorganic aerosols have increased 1−5 % per decade over 1979−2001 due to climate change alone. CTM simulations using meteorology from regional climate models indicate that ozone will increase by 10−20 % in summer in southern and central Europe during the coming 30 years just because of climate change. For secondary inorganic aerosols, model studies indicate a larger increase in most of Europe during most seasons. The increase in Europe could be 10−30 % over 30 years. (Year-to-year variability in emissions are not accounted for). On a decadal scale the climate change signal in the ozone and PM concentrations is comparable to or larger than the signal due to meteorological variability.

Are changes in air quality arising from emission control measures larger than or less than the changes in air quality that may arise from climate change?

Change in air quality, *e.g.* ozone, sulfates and nitrates observed during the last 50 years, is shown to be significantly influenced by climate change and is thus important to take into account when evaluating the actual effect of different control measures. For some parameters, climate change affects mainly the transport pattern and thus mainly change the "effect" pattern, while for others, like ozone, climate change increases the formation and thus the actual concentrations and the total effects. Several air quality components, for example, ozone, black carbon and aerosols, are shown to have significant effect on the climate. These components have shorter lifetimes in the atmosphere than most of the greenhouse gases. Climate strategies for a short time horizon (a few years) counteracting rapid climate change should be coordinated with air quality measures as several of these components have considerable health effects. Methane is the one greenhouse gas with short life time that should be considered for climate abatement on a short time scale. Control measures concerning greenhouse gases and other climate relevant parameter for counteracting climate change will most certainly affect air quality not only due to climate change but even more as the same sources will be controlled, *e.g.* combustions sources.

Will regional emission changes affect regional climate? Will air quality emission reduction policies lead to emission changes that counteract climate change policies?

If the global radiative forcing effect of anthropogenic aerosols is 1–1.5 W/m^2 as suggested by IPCC then the down wind effect of reducing emissions should be noticed in the regional climate. The magnitude and character of the climate change effect has to be analysed by regional air quality and climate models and observations in combination. The models need to include a sufficient description of the relevant air quality parameters. A large reduction in emissions of particulate matter and particulate matter precursors will most likely intensify climate change and thus on a short time scale counteract climate change reduction policies. Regionally very large increases in radiative forcing are to be expected as aerosol burden declines, the current radiative forcings by particulate matter can be identified in connection with biomass burning over Amazonia and in the Indoex experiment. A targeted reduction in ozone precursors or black carbon can reduce regional warming.

Regional air quality models need to be coupled with climate change models to include air quality parameters and to interact, such that air quality models can take into account climate change and *vice versa.*

Future outlook

In a policy context (*e.g.* EU or CLRTAP - EMEP) it is required to account for how climate change contributes to air quality changes and how air quality changes contribute to regional climate change. This implies a need to integrate climate change and air quality communities. The climate change community has up to now focused on how weather elements and their probability density functions change with time and location as a consequence of increasing radiative forcings from greenhouse gas and particulate matter concentration changes. Further the climate change community has focused on the societal implications of the changed probability density functions of weather elements, but, up to now, air quality has not been part of the picture. This comment is addressed to the science community: policy makers and the research community needs to have a good showcase, see CLRTAP + UNFCCC.

Joint assessment by IPCC and the global air quality-body (CLRTAP) must be made global and rooted in the science plus policy arena. An example is that the Montreal protocol technical body and IPCC together prepared a stratospheric ozone-climate assessment.

The science community findings of air quality and climate change interlinkages should be published in publications that are common ground to both air quality and climate change research communities.

Coupled climate-chemistry models should be developed in a stepped approach with time, as base information evolves. As base information is meant *e.g.* dynamical description of two way fluxes between land and the atmosphere and between ocean and the atmosphere with appropriate resolution and accuracy. Another constraint on the pace of the coupled climate-chemistry model development is the evolution of resources like computer power, and the evolution and availability of observational material from *in-situ* and remote sensing instrumentation. To the science community, an important time post will be the next IPCC assessment (start in 2009). This is also addressed to international research and coordination structures like IGBP and WCRP/WMO.

Emission estimates and scenarios

Harmonisation needs to go beyond 2020 which has been established through the Clean Air for Europe Thematic Strategy and needs to include the major greenhouse gases and air quality pollutants and include particulate matter and their precursors as well as heavy metals and persistent organic pollutants. As climate models and air quality models are being coupled, the demand for resolution of emission estimates increases (0.1 × 0.1 degree?).

In Table 1 below examples are given of important physical parameters for atmospheric composition, and where different aspects of the parameters are in focus in air quality calculations and weather forecasting. Further research is needed to assess the PDF properties of these parameters in an atmospheric composition context.

Table 1

Parameter	CTM	NWP
Wind speed	Stagnant conditions	High wind speeds
Wind direction	Essential for S-R-relationships	Not so important
Precipitation	Length of dry periods; low intensity rain	Heavy rain
Temperature	High temperatures – fast reactions and large biogenic emissions	High and low temperatures, freezing
Clouds	Type, location, lifetime	Cloud cover
Convection	BL ventilation	Precipitation
τ BL,res , Hmix	Important	Not so important
Specific humidity	Important for [OH]	Not so important
Ground surface	Important for q, deposition, biogenic emissions	Important for fluxes of heat, momentum, moisture

Acknowledgements

A large part of this text derives from the discussions at the "Saltsjøbaden 3"-conference "Air pollution and its relationship to climate change and sustainable development. Linking immediate needs with long term challenges" in Gøteborg 12th-14th March 2007, in the working group on "Climate change and air pollution – a long term perspective", summarised and chaired by Øystein Hov (see Grennfelt).

[Grennfelt, P., L Lindau and J Arnell (2007) Air pollution and its relationship to climate change and sustainable development. Linking immediate needs with long term challenges. IVL 30 May 2007.].